Ana Isabel Morais Lavrador Pereira
Licenciada em Conservação e Restauro

The perfect paint in Modern Art Conservation: A comparative study of 21st century vinyl emulsions

Dissertação para obtenção do Grau de Doutor em
Ciências da Conservação

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FACULDADE DE CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

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Aknowledgements

To my dearest Tio Chico, the last steps were made under grieve because of your sudden disappearance but, I kept on going because I knew you would be very proud of me if I finished.

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"… my colour palette got narrower merely because I chose it to be like that.
Colours did not interest me. I think they distract me from the essential.
You start paying to much attention at the yellows, pinks and so on
which may be important for some people
but, not for me..."
JULIÃO SARMENTO

Abstract

Contemporary painting places, and will continue to place, several questions about its meaning, its chemical nature, its durability and the best way to preserve it. This research aims at putting together comprehensive data on vinyl based paints, including their components, their properties, their aging behavior and their response to selected cleaning products.

In this project degradation mechanisms of vinyl binders and formulations used in the 20th and 21st century were studied. Stability over time of selected vinyl polymers was assessed through natural indoor and artificially aging. The objective was to enhance knowledge and understanding of vinyl emulsion formulations and their performance over time.

Overall conservation state of pictorial layers namely, adhesion, cohesion and discoloration of selected case studies from the Portuguese artist Julião Sarmento (b.1948) was correlated with the observed molecular level changes studied in laboratory experiments. Sarmento's paintings were chosen due to conservation concerns (discoloration) on some of his works from the 90's. Besides, research was carried out to start increasing the knowledge of what can be expected of PVAc based paints in terms of response to conservation treatments namely, surface cleaning.

Artificial aging showed that the most recent formulations which are based on a poly(vinyl acetate), poly(vinyl chloride) and polyethylene terpolymer are less stable when compared to some homopolymer formulations. From the four pigments studied, titanium dioxide rutile and a carbon based black proved to be stabilizers for both types of polymer. The mixture lithopone plus calcium carbonate has showed to have a photocatalytic effect on the binders.

The studied paintings showed to be in an overall good state of conservation except for the paintings created in the 90's with white glue and a mixture of white lithoponeand calcium carbonate. Discoloration of this white paint seems to be irreversible and ongoing and is still a major concern. The disapearance of the plasticizer was the only change detected. The current works created by Sarmento are expected to be more stable as they were painted using the rutile titanium dioxide.

Immersion/cleaning tests showed that vinyl based paints can be susceptible to water and organic solvents like ethanol as some evidences point to the removal/diffusion of additives from the paint. The observations made point to the need to further proceed in this research field.

Keywords: contemporary paintings; poly(vinyl acetate) emulsion paints; photodegradation; discoloration; cleaning.

"… a minha paleta de cores ficou mais restrita por opção.
Essas cores não me interessam. Acho que me distraem do essencial.
Começa-se a olhar para os amarelos, para os rosas e por aí fora.
O que pode ser importante para algumas pessoas
mas, não para mim..."
JULIÃO SARMENTO

Resumo

A pintura contemporânea coloca e continua a colocar diversas questões relativamente ao seu significado, à natureza química dos materiais utilizados, à sua durabilidade e qual a melhor maneira de a preservar. A presente investigação tem como objectivo reunir dados sobre tintas sintéticas vinílicas incluindo os seus componentes, as suas propriedades, o seu padrão de envelhecimento e resposta a alguns produtos de limpeza comunement usados em conservação.
Neste projecto mecanismos de envelhecimento de aglutinantes vinílicos e tintas usados no século XX e XXI foram estudados. A estabilidade ao longo do tempo de alguns polímeros vinílicos foi avaliada através de envelhecimento natural e envelhecimento acelarado a fim de, contribuir para o conhecimento e compreensão da formulação destas tiintas e do que se pode esperar delas ao longo do tempo.
O estado de conservação das camadas pictóricas nomeadamente no que diz respeito à adesão coesão e alteração da cor de casos de estudo selecionados a partir da obra do artista português Julião Sarmento (n.1948) foi correlacionada com as alterações a nível molecular detectadas nas experiências conduzidas em laboratório. As pinturas de Sarmento foram escolhidas devido a problemas de conservação detectados nomeadamente, amarelecimento de algumas das suas obras dos anos 90. Além disso, a investigação conduzida quis ser um ponto de partida para reveler o que se pode esperar das tintas à base de PVAc em termos de resposta a alguns tratamentos de conservação nomeadamente, à limpeza de sujidade superficial.

O estudo feito em envelhecimento acelarado revelou que as formulações mais recentes baseadas no terpolímero de polivinil acetato, cloreto de polivinilo e polietileno são menos estáveis que algumas das formulações que contêm o homopolímero de polivinil acetato. Dos quatro pigmentos estudados o dióxido de titânio na forma rutilo e um negro à base de carbono estabilizaram o aglutinante. A mistura de litopone com o carbonato de cálcio mostrou ter um efeito catalítico na fotodegradação dos polímeros.

A observação e análises das pinturas de Julião mostraram que no geral estas estão em bom estado de conservação à excepção das obras criadas nos anos 90 com cola branca e litopone. O amarelecimento desta tinta branca parece ser irreversível e contínuo e é ainda objecto de preocupação. A nível da composição da tinta observou-se o desaparecimento do plasticizante. Maior estabilidade deve ser apresentada por obras mais recentes já que foram pintadas usando branco de titânio.

Testes de imersão/limpeza em algumas das tintas de base vinilica apontaram como estas podem ser sensíveis a solventes orgânicos como o etanol e a água ao remover ou provocar a difusão de aditivos das tintas. Os resultados indicam a necessidade de prosseguir com a investigação nesta área.

Keywords: pintura contemporânea; tintas aquosas de acetato de poli(vinilo); fotodegradação, amarelecimento; limpeza.

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Preamble

When a Conservator-Restorer is faced with the responsibility of caring for contemporary paintings there are several questions that are raised: what is the used material, how does it age and how does it behave in particular exposure, handling, storage and treatment conditions. Conservation science has the analytical means and should contribute by providing the needed answers.

The variety of artist's materials and techniques has grown with the development of industry and artist's freedom of choice has gone along with it. Awareness of these changes and concern over its consequences, by conservators and conservation scientists, has increased and widen research to include: unfolding the contexts and reasons for the artist's choice; identifying the materials used; studying the properties and aging behavior of those materials; and, unveil the material's response to conservation products and treatments.

Waterborne or water thinnable paints usually referred to as emulsion paints were developed in the 1950's with the aim of replacing the comon organic solvents by water.[1] Popularity of this environmentally friend emulsions grow rapidly and continues to grow among coating formulators and end-users because of their well-know advantages namely safe handling, low toxicity and fast drying. In the mid 20th century synthetic emulsion based paints appeared in the market [2] and by 1965 most artist's paint makers were selling their own brands of latex paint.[3]

With synthetic paints artists could create works of intense colour and elasticity, the material was easy to manipulate as was thinned with water and could be applied directly on to any support.[4] Large areas of color could be created maintaining color and texture uniformity and the artist's brush mark could be avoided. Either in the form of industrial products (household paints) or, artist's paints, synthetic paints have ruled the market since their introduction and achieved progressive popularity among artists. As knowledge of the properties and aging behavior of the paint's binding medium is invaluable to understand, preserve and treat works of art [2] artist's widespread use of waterborne based paints has been the subject of concern and one of the focus of research in the conservation of contemporary paintings.

Vinyl paints have been used by Portuguese artists at least since the early sixties. Performance of these paints regarding it's stability in the short and long term and adequate preventive measures and treatment is presently a subject of research and of interest for conservators and conservation scientists in Portugal. Based on photodegradation quantum yields it has been concluded that some 20th century PVAc formulations based on the homopolymer present high photostability.[5,6] The results are in agreement with the results obtained for paintings of Portuguese artists like Ângelo de Sousa (1938-2011) and Joaquim Rodrigo (1912-1997) two of the first artists to surrender themselves to the advantages of these new synthetic paints in the early 60's.[5, 7] The naturally aged paints from works created by these two artists are in good condition, with no signs of physical changes or chemical degradation and the results obtained in their analyzes are in agreement with artificial aging experiments which indicated that applied as a solution, emulsion, or coloured paint, the homopolymer is very stable to light.[7]

In this project we will study the composition and characteristics of other 20th century paint formulations based in PVAc co and terpolymers. Additionally we studied the ageing mechanisms, at the molecular level of 21st century vinyl terpolymers used as binding media in artists' paints in Portugal.

Selection of the products to be studied followed the materials and techniques used by the Portuguese artist Julião Sarmento (b.1948). Over his artistic career, Sarmento has used different vinyl paints embrassing the great advantages of their technical properties that allowed him to incorporate different aesthetic values into his works. Sarmento is one of the most prominent Portuguese contemporary artists. Working since 1975 Julião made and continues to make broad use of several vinyl paint systems, manufactured by Portuguese or international companies. His paintings are therefore paradigm case-studies, suitable to investigate vinyl paint components, characteristics and their aging behavior. Moreover, Sarmento's paintings from the 90's are of special concern due to reported evolving degradation problems. In the 1990's he started a series of works, commonly referred as *White Paintings*, due to their vast monochromatic backgrounds of symbolic and neutral color, over which he drew ambiguous figures depicted in black. Paints from this period are homemade and consist typically of lithopone plus calcium carbonate (*Cenógrafa* dry pigment) mixed with a PVAc white glue (*Vulcano V7*) (both products produced by *Favrel Lisbonense*, a Portuguese artist's materials company[1]). The aesthetic of these works has changed due to the development of discoloration (yellowing) in the uppermost surface.

Seeking to provide helpful guidelines for practicing conservators, research was conducted in order to start to uncover vinyl paints' response to specific products commonly used in surface cleaning. As before the materials to be studied were chosen according to the materials used by Sarmento. Furthemore artificially aged samples were used in immersion tests. Aging of vinyl paints may result in a diferent molecular structure giving the material diferent characteristics from the original ones. Therefore the impact of cleaning can be diferent from the one when unaged paints are tested. Naturally aged samples provided by the artist were also studied. The results show that vinyl paints can be affected by some of the cleaning products tested.

[1] In business since the eighteen century this company is the oldest Portuguese fine arts materials company to produce paints for artistic use.[5] Although it was founded in Oporto in 1891 the business was transfered to the branch created in Lisbon.[5]

~ Part I ~

Polyvinyl acetate paints: characterization, conservation concerns and stability/degradation behaviour

I.Introduction

1.1. Poly(vinyl acetate) emulsion paints: formulation and use

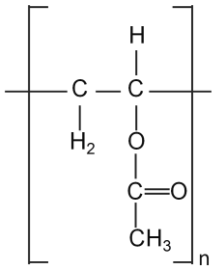


Fig.I. 1: Chemical structure of poly(vinyl acetate)

Although the subject of synthetic based paints is vast and complex, four main classes were used as the binding medium either as household paints or, artist's materials: acrylic, alkyd, poly(vinyl acetate) and nitrocellulose.[8] Within these four classes acrylic and vinyl emulsions were the most important synthetic paints used by artists in the twentieth century.[8] Even though the first commercial emulsion paints appearing in the market were based on poly(vinyl acetate) (Fig.I.1) [2], presently in the 21st century, acrylic artists' paints dominate the USA market.[6] PVAc homopolymers were used in the first commercially produced emulsions in the 1930s[8] and together with PVAc copolymers[2] they are still important and widely used binders in household paints industry.[2,10] Their importance as a raw material in the water based paints and adhesive industry is due to its attractive cost-performance features.[1,9, 11-13] Vinyl dispersions are usually described as forming transparent films that are lightfast and that have a good adhesive strength.[1]

The first artist's waterborne vinyl paint was developed in 1946 by the *Borden Company* (United States of America) and was named *Polymer Tempera*.[14] Other manufacturers produced PVAc paints designed for artists used since 1960. PVAc based paints included *Hyplar Artist's Colours* produced by *Grumbacher* (USA) [15]; the *New Masters* vinyl-acrylic copolymer based paints produced in the *Old Holland* factory (Netherlands) [8]; the *Spectrum* line based in a PVAc homopolymer produced by *Spectracryl* (United Kingdom) [16] and the *Rowney PVA Colours* manufactured by *George Rowney & Company* (UK) with a PVAc homopolyer. All these paints have been discontinued except for the *Flashe* PVAc-VeoVa copolymer based paints produced by *Lefranc & Bourgeois* (France).[2; 17] In Portugal the *Sabu tempera* colours and *Geo* fluorescent paints were vinyl aqueous paints produced by the *Favrel*. *Kreme*r (Germany) also produces a line of PVAc paints designed for conservation use. Designated as *Golden PVA Conservation Paints* they are made with PVAc dissolved in ethanol.

[2] A polymer is a large molecule made up of smaller repeating units, the monomers. If the polymer only contains the same repeating unit it is called a homopolymer. If different monomers are present than it is called a copolymer. If a copolymer is prepared from three different monomers, terpolymer is the designation used. A blend is a mixture of different polymers. [18]

Vinyl paints produced in Portugal came into market in the 50's and become an important material resource of artistic expression for Portuguese painters since the 60's.[5,18] At least from 1954 the Portuguese paint manufacturer *Robiallac* produced a series of household paints based on vinyl emulsions.[5] Vinyl colored and pure binders for artistic purposes were first produced in the late 50's by *Favrel Lisbonense*. With a long tradition in the production of artist's materials this was the first Portuguese fine art material company (manufacturer) to introduce these paints in Portugal.[5] *Favrel*'s products could be purchased at the store Casa Varela (a shop run by the factory). Production and trade of these products ceased completely when *Favrel* closed in December 2006 and the store closed in 2011. Among them were the *Sabu* colored paints and the white glue *Vulcano V7*.[5,18]

1.1.1.Chemistry of PVAc emulsions

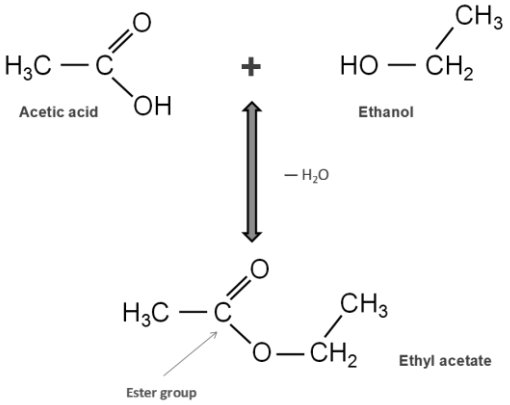


Fig. I.2 : Synthesis of ethyl acetate from acetic acid and ethanol.

Poly(vinyl acetate) is obtained from the monomer ethyl acetate or ethyl ethanoate $CH_3COOCH_2CH_3$ an ester that is formed by a condensation reaction between acetic acid and ethanol with formation of water as a byproduct.[18] (Fig.I.2) The monomer can be polymerized by free radical methods in a chain reaction (addition polymerization) in which the molecular weight increases by successive linking of monomer molecules to the end of the growing chain.[11, 18]

The process involves three major steps: initiation, propagation and termination. The initiator catalyzes the reaction by generating free radicals that react with the unsaturated carbon-carbon bonds containing monomer. When the initiator radicals and monomer react a larger free-radical is formed which in turn reacts with another monomer molecule, thus propagating the polymer chain. Growing polymer chains are terminated by reacting with another free radical or, (for instance) with chain transfer agents or inhibitors. The final polymer is a an amorphous, thermoplastic polymer.[20]

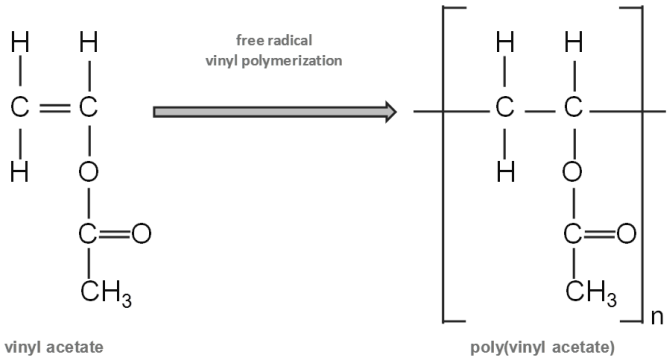


Fig.I. 3: Polymerization of vinyl acetate through free radical mechanisms

Vinyl dispersions are generally produced by chain-growth in emulsion polymerization (Fig.I.3) a process that is widely used for manufacture of latex paints and adhesives because the emulsified product can be used directly.[1, 11] A typical emulsion polymerization formulation involves four basic ingredients: the monomer, a dispersion medium, an emulsifier[3] and an initiator.[20] The vinyl acetate monomer is dispersed in water by the emulsifying agent in the form of micelles. Initiator radicals diffuse into the micelles and cause monomer molecules to polymerize. As the polymerization continues more monomer molecules migrate into the micelles and termination occurs by radical combination. When the polymerization is complete, a stable colloidal dispersion of polymer particles in an aqueous medium (the latex) will remain.[1,11,20]

The most commonly used initiators in emulsion polymerization of VAc are water soluble, thermally decomposed, free-radical producing persulfates (peroxodisulfates) such as potassium, sodium, and ammonium-persulfate.[20, 21] Generally mixtures of nonionic (eg. polyethoxylate based products) and anionic emulsifiers (eg. sodium, potassium and ammonium salts of fatty acids) are used.[20] The emulsifier content is typically between 2-6% by weight.[21] Stable PVAc latexes can only be made with the use of protective colloids like poly(vinyl alcohol) and hydroxyethyl cellulose.[20] These two polymers are common in the polymerization of VAc to increase the particle stability and avoid particle coagulation.[21] As water-soluble polymers they can be used in the presence of the emulsifier and a typical content is between 1 to 10% by weight.[4]

The final product comprises polymer macromolecules suspended in water as minute (within the size range 10nm to 1000nm in a diameter [20]), spherical particles coated with an extremely thin layer of emulsifier. In emulsion polymerization it is possible to produce high molecular weight (M_w) polymers generally with values above $1x10^6$.[21] Because the viscosity of a latex produced by this method is independent of the polymer's molecular weight, emulsions can present a high solids content with low viscosity.[20] In general emulsions contain 40-60 % of polymer solids dispersed in the aqueous phase.[20]

[3] Emulsifiers are also referred to as surfactant, soaps, dispersing agents, and detergents. These are surface active molecules with a long-chain the hydrophobic group and a hydrophilic group.

1.1.2.External plasticizers: the phthalates

Minimum film forming temperature (MFFT) and glass transition temperature (T_g[4]) of vinyl emulsions depend on its molecular weight. For a medium molecular weight a PVAc dispersion's T_g is approximately 30ºC and its MFFT is approximately 20ºC.[20] That makes poly(vinyl acetate) polymers slightly too hard and stiff to perform as effective binders for pigments at normal ambient temperatures.[20] Therefore formulations have either to include external plasticizers, in quantities up to 20% by weight of polymer, or to be obtained from copolymerization with softer monomers.[2] Until the 60's external plasticizers were used for this purpose.[2]

Plasticizers are added to the system to change physical properties by increasing polymer's flexibility, workability and reducing its viscosity.[11] Plasticizers lower film-forming temperature and are chemically inert as they do not react with the binder.[1] Typically plasticizers are low molecular weight molecules with high viscosity and high ebullition point (low volatility) that increase free volume by surrounding polymer macromolecules and keeping them apart.[1]

Phthalates are phthalic acid esters (dialkyl or alkyl aryl esters of 1,2-benzenedicarboxylic acids) (Fig.I.4) which are commonly used in the polymer industry due to their stability, fluidity and low volatility [22] and represent approximately 90% of the plasticizers used annually in Europe.[23] Dibutyl phthalate holds a dominant position as a plasticizer for PVAc dispersions.[24, 25] However it seems that health constraints have lead to a decrease in the use of DBP while for instance diisobutyl phthalate (DiBP) is still permitted to be used.[5]

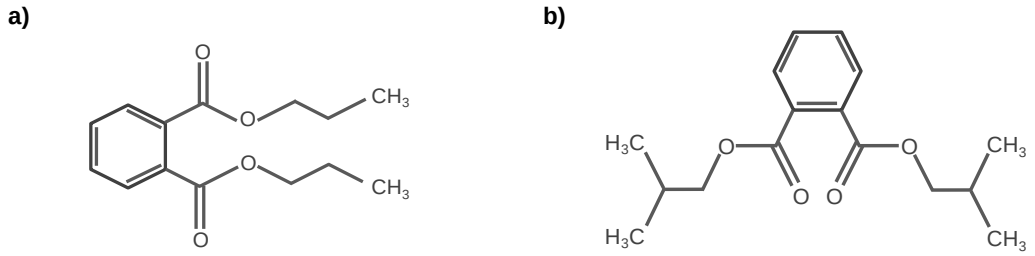


Fig. I.4 : Chemical structures of a) dibutyl phthalate (DBP) and b) diisobutyl phthalate (DiBP)

[4] Tg: glass transition temperature; temperature at which the polymer swichs from a solid to a liquid. Above Tg the polymer appears to be a liquid melt and has a rubbery behavior while below Tg the polymer acts as a glassy solid (relatively rigid and brittle). Around the transition the polymer will act as a deformable solid or, a soft glass. [12,18] Below Tg, the polymer molecules are more or less randomly close packed and as the temperature increases the amplitude of the molecular movement increases and the polymer expands. [11,18]

[5] The use of DBP and DiBP in Europe has been limited to specialised applications by REACH, the Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals which streamlines and improves the former legislative framework on chemicals of the European Union. DBP, BBP and DEHP were determined according to the REACH regulation to be phased out by February 2015 unless an application for authorisation is made before July 2013 and an authorisation granted.

1.1.3. Internal plasticization: copolymers

Because external plasticizers molecules are not attached to the polymer chains by primary bonds they can be lost by evaporation, migration or extraction leading to concern of embrittlement of the films after a relatively period of time.[1,24] Due to this impermanence plasticization of the polymer by copolymerization replaced the use of external plasticizers.[2] In this case the flexibilizing moiety is chemically bonded to the polymer and is called internal plasticization.[11] For plasticization purposes usually a softer monomer is combined with the harder VAc monomer. The most important comonomers used in vinyl emulsions are vinyl laureate, dibutyl maleate, versatic acid esters, ethylene, vinyl chloride and butyl acrylate.[1] Emulsions of copolymers of vinyl acetate with dibutyl maleate are referred as being significant in the exterior house paints industry in the 60's.[26] Copolymerization of VAc with softer monomers like acrylics has also been done since that decade.[11]

Nowadays, emulsions of vinyl acetate-vinyl versatate (versatic acid esters) copolymers are generally recognized as leading latexes in interior and outdoor industrial paints (Fig.I.5).[13] Vinyl versatate polymers are long–chain branched vinyl esters obtained by polymerization of the vinyl neo-decanoate monomer ($C_{12}H_{22}O_2$) and are also known as VevoVa 10 or, in the case of the monomer Neo-10.[9] The manufacturing process of these highly branched tertiary monocarboxylic acids was developed by Shell Chemical Company over 30 years ago.[9] The various VeoVa products differ in the degree of branching and in the length of the hydrocarbon chain. For instance, neo-9 (vinyl neo-nonanoate monomer, $C_{11}H_{20}O_2$) and neo-11 (vinyl neo-undecanoate monomer, $C_{13}H_{24}O_2$) were introduced by the company under the trade name VeoVa 9 and VeoVa 11.[9] VeoVa 10 is the most commonly monomer and is used advantageously in vinyl acetate based latexes and paints to improve scrub resistance, gloss and hydrophobicity.[13] Polymerization of these branched vinyl esters with VAc results in polymers whose hydrolytic stability improves with increasing concentrations of branched vinyl ester.[20] The bulky nature of these side groups protects the neighboring vinyl acetate segments and increases the hydrolytic stability[6] of the resulting copolymer.[9] Diversity in chain length and degree of branching results in a wide range of T_g, in general lower than that of PVAc therefore they can act as efficient plasticizers.[7][9] Typically, interior paint latexes tend to contain 15-20% of VeoVa monomer and latexes for exterior apllications usually contain 20-30% of the branched monomer. [20]

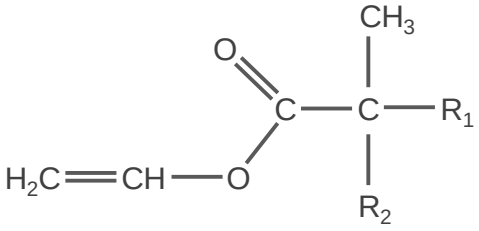


Fig. I. 5 : Structure of VeoVa monomers where R1 and R2 are branched alkyl groups containing 6 or 7 carbon atoms for VeoVa9 and VeoVA10 monomers respectively.

[6] Ability of a substance to resist chemical decomposition (hydrolysis) in the presence of water.
[7] For instance while the VAc monomer has a Tg of 30ºC the vinyl neo-decanoate (neo-10), vinyl neo-undecanoate (neo-11) and the vinyl neo-dodecanoate (neo-12) have a Tg of -3, -40 and -3ºC respectively.[9]

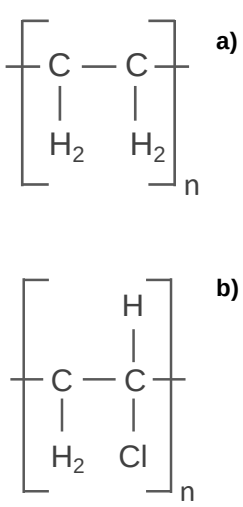


Fig. I.6 : Chemical structures of a) poly(ethylene) and b) poly(vinyl chloride).

Copolymers of polyethylene (PE) (Fig.I.6.a) and vinyl acetate are commercially important and are used as adhesives and as coatings.[11] Changes in the VAc content causes variations in its properties such as crystalline and impact strength.[25] Copolymers of poly(vinyl chloride) (PVC) (Fig.I.6.b) and poly(vinyl acetate) are an important example of PVC copolymers used in paint technology [1] and are mentioned since 1964 as paint binders included in the growing and rapidly developing paint's industry.[26] Vinyl chloride polymers are tough, abrasion resistant, thermoplastic although they have to be stabilized against dehydrochlorination in the presence of heat and/or UV radiation.[1] The usual way is to add adequate light stabilizers (e.g. UV absorbers).[27] Protective coatings that filter the harmful radiation have been sucessfuly tested as means to protect the PVC underlying polymer.[27] Other strategies include copolymerization or blends with other polymers.[28] Recent vinyl formulations have been developed for increasing stability in solution and as interior paints. Films formed by the vinyl acetate-vinyl chloride-ethylene terpolymer, P(VAc-E-VC) are considered to be more resistant to hydrolysis than PVA homopolymer and other copolymer dispersions and are also claimed to possess a higher mechanical strength.[1] Besides these copolymers also present a good cost-performance ratio.[1]

1.1.4. Colored emulsion paints formulations

Waterborne emulsions are complex chemical systems because extra formulation components namely, additives are necessary to improve mechanical stability, binding capacity and shelf lifetime among other purposes.(Table I.1) For instance, PVAc emulsion systems are sensitive to changes of pH and the optimum pH range (pH=4.5—5.5) can be generally achieved by using buffers like sodium bicarbonate (sodium hydrogen carbonate, $NaHCO_3$).[20] The purpose of a particular additive can be twofold. As has been mentioned protective colloids are added for dispersion stabilization however they also promote control on the latex rheological properties.[9]

Colored latex paints are even more complex than the raw emulsions used. A paint is a composite made of a binding medium, a dispersing agent, pigments, fillers and additives. Paint formulators can use a host of additives to obtain a latex paint to modify certain properties during manufacture and storage. Others may be added to the system to fulfil artist's demands in terms of finishing appearance. Technical properties like drying time, surface finish, viscosity, texture and pigment load are manipulated with additives.(Table I.1) Although their amount in a coating formulation is seldom more than 5% by weight additives can have a major influence in various paint properties on the short and long term.[1, 29]

Dispersion and stabilization of pigments in polymer dispersions is somewhat difficult since dispersions form a continuous phase in water and uniform distribution of the dispersed pigment particles in the paint is hindered by coalescence of the polymer particles.[1] To overcome that

problem additional surfactants have to be added to the system. These wet the pigment surface by preferential adsorption by the hydrophobic end while the hydrophilic end orientates itself to the water. The amount of surfactant needed depends on the total surface area of the pigments present.

As has been said for two different goals the same additive can be used. Another example is diethylene glycol butyl ether (butyl diglycol) a commonly used coalescing agent that also acts as temporary plasticizer because it is required to be volatile and diffuse and evaporate from the film upon drying.[29] Furthermore, for the same purpose a mixture of additives can be used. Thickening agents are used to tailor paint consistency, avoid settling of the pigment and assist in the layer thickness. Cellulose derivatives are commonly used as protective colloids but they also act as thickeners for PVAc emulsions and for a better performance paint manufacturers often use two cellulosic thickeners of different molecular weight.[30]

Table I.1: Formulation of emulsion paints including additives used during emulsion production and paint manufacture. [1, 3; 29, 30, 31]

Formulation	Component purpose
	Emulsion
Water	Dispersion medium
Polymer	Binder
Surfactant	Wetting agent that promotes dispersion of the polymer particles
Protective colloids	Increase the stability of the dispersion
Adhesion promoter	Promotes the adhesion of the binder on the surface[8]
Initiator (residual)	Residual polymerization components
Buffer	Maintenance of pH
Preservatives (biocides)	Protection against growth of microorganisms
Antioxidants; UV absorbers	Improve light stability; prevention of degradation.
	Paint
Pigments	Coloring agent
Fillers	Improvement of application; cost reducing
Antifoam[9]	Inhibits air entrapment
Thickeners	Improves viscosity
Freeze-thaw stabilizers	Avoids freezing in cold environments
Wetting agents	Spreading ability
Pigment dispersants	Promotes pigment suspension and reduces flocculation
Preservatives (biocides)	Protection against growth of microorganisms
Coalescent agent	Film formation promoters
Buffers	Maintenance of pH

[8] Organo functional silanes are the most commonly refered adhesion promoters. They impart improved 'wet adhesion' on non porous substrates.
[9] Antifoam substances are used to rupture the bubbles naturally formed during the drying of the film before the fusion of the latex film. Examples found to be sold in the industry are: blends of mineral oil with silica derivative and mineral particles.

Our knowledge regardind the additives that can be found in vinyl paints is starting to grow. Doménech-Carbo et al. have been able to identify some of the additives in selected artist's vinyl paints: cellulose ethers usually used as thickeners, methenamine used as a preservative, phosphate compounds used as flame retardant and surfactants of non-ionic polyethylene oxide type were all identified in an artist's vinyl commercial based paint.[32]

1.1.5. Drying mechanism of emulsion paints

Film formation from a latex, a process by which an aqueous dispersion of polymer particles transforms into a continuous material, is a complex process and a unifying mechanism that convinces the whole scientific community has yet to be presented.[33]

Subject reviews show general agreement that three major stages occur: concentration, compaction and coalescence.[29; 33-34] (Fig. I.7) During stage one water evaporates from the paint's surface leading to approximation and ordering of the solids content. Stage two begins when the polymer latex particles first come into irreversible contact leading to particle deformation. The formation of the continuous film is usually referred as stage three and involves polymer interdiffusion. It is during this final stage that the latex becomes more homogeneous and gains its mechanical properties as polymer chain interdiffusion occurs and particle interfaces tend to become less distinct. 'Coalescence' (i.e. compaction, deformation and polymer chain interdiffusion) occurs when stabilizing forces (electrostatic and/or stearic), resulting from the charged polymer chain end groups or adsorbed surfactant/polymer, keeping the individual latex particles held are overcome.[29; 33-34]

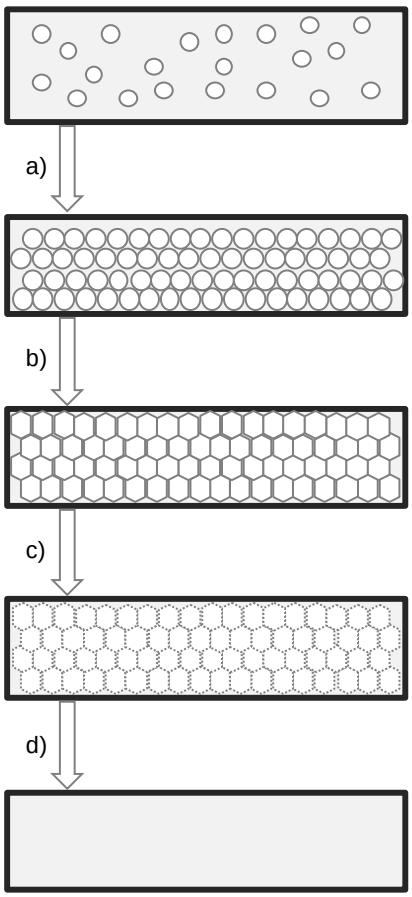


Fig.I. 7: Simplified image of the drying mechanism of an emulsion. a) concentration and orientation of polymer particles b) deformation, beginning of coalescence c) coalescence and starting interdiffusion d) interdiffusion and the resulting homogeneous film

The formation of a continuous material depends on the MFFT of the polymer, which in turn is dependent on the elastic modulus (resistance to particle deformation), and, to a lesser extent, to the viscosity of the polymer.[33] If the film is cast above its MFFT, the polymer particles are sufficiently soft for deformation and cohesion of the latex particles to occur.[33] Interdifusion of polymer particles (a requisite to obtain a strong, continuous film [34]) increases with temperature and decreases with increasing molecular weight.[29])

There are in fact many factors mentioned in the literature that work against interdiffusion such as:

polymer hardness; large polymer particles; emulsifier content; the presence of protective colloids; unsuitable pH; application over porous substrates. Polymer hardness can act against complete particle interdifusion because hard particles deform very little and are unable to take part in the coalescence process.[29] Extra complexity in film formation is caused by additives.[33] Surfactants are known to affect several aspects of film formation and the rate and degree of polymer diffusion is one of them.[34] These additives may be compatible with the bulk polymer or, they may phase separate migrating to the surface or, can be entrapped at polymer particle surfaces forming a continuous network. The formation of this separate phase of surfactant may hinder the coalescence of the polymer.[35] This effect has been seen by Zumbühl et al.[36] in acrylic latexes and will be discussed further on. Drying conditions can also affect the drying process. If there is quick water removal the latex particles loose mobility and cannot move to achieve proximity for coalescence.

1.2. Concerns over the photostability of synthetic binding media

The stability of a coating is influenced by a number of factors. The intrinsic chemical and physical nature of the polymer; the environment at which it is exposed namely, light, temperature, humidity and atmosphere; the chemical nature, physical characteristics and concentration of pigments and fillers; and the presence of additives.[37]

Jablonski et.al. summarized the main conservation concerns raised by the use of synthetic paints.[4] The authors underlined the need for a full understanding of the complex structure and components of the paints; of its aging mechanisms and consequences; of the influence of external factors in paintings conservation state and the implications of conservation treatments.[4] Regarding acrylic paints, systematic studies have been undertaken in the last decades that resulted in the proposal of multi analytical methodologies for the characterization of paint formulations. A recent review by Learner et al, enumerates the main findings from studies in the degradation of acrylic based paints: their stability tendency with the exception of a common migration of some additives and a slight level of cross-linking and chain scission. As a consequence there could be an increase of the paint layers stiffness with time. Additive migration and deposition on paint's surface can also lead to changes in the surface appearance as for instance loss of gloss and a haziness effect.[10]

Research on PVAc paints photostability including systematic paint system characterization and degradation studies have been carried out and important conclusions have been published.[6, 16,18, 32, 38-39] A first systematic study of the materials used by selected Portuguese modern and contemporary artists has been carried out.[5] Lia et al, found that the vinyl waterborne paints studied when subjected to light undergo loss of phthalate plasticizer and that polymer chain scission is the main degradation pathway.[5,6,38] The sensitizing effect of some pigments and protective effect of others on the degradation level of PVAc was also showed in these studies. Doménech-Carbó's research group has carried out a thorough identification of the components used in some vinyl based commercial paints and has concluded that irradiation with short wave UV light leads to a decrease in the plasticizer content. Moreover oxidation and chain scission of the

polymer was detected.[16,39] Besides, plasticizers have been shown to support the growth of some microorganisms in PVAc paints. [40]

As already described since the 60's PVAc has been copolymerized with softer monomers to achieve a lower T_g. [2] And as the studies mentioned above point to the fact that PVAc homopolymer emulsions are stable and resistant to light, to the best of our knowledge there are no publications dealing with the molecular level evolution of vinyl formulations developed and used from the last decades of the 20^{th} century. As it was mentioned vinyl terpolymer formulations are considered to be more resistant to hydrolysis than PVAc homopolymer and copolymer dispersions and they also possess an higher mechanical strength.[1] These terpolymers were one of the raw emulsions used to produce the *Sabu* vinyl artists paints and these have been used, since the fifties by Portuguese artists. However there is no reference on lifetime improvement an important requisite to be used in Art particularly taking into account the sensibility of poly(vinyl chloride), PVC, to light [27, 41-53] that makes it the least weathering-resistant of the important industrial polymers used in outdoor applications.[27] Therefore one of the objectives was to study the emulsion's stability and the effect of pigments in P(VAc-VC-E) artists' paints and to compare the photostability of these paint systems with systems based on the homopolymer white glue *V7* as well as with poly(methyl methacrylate (PMMA) considered one of the most photostable acrylic polymers [54].

1.2.1. General mechanism of photodegradation of synthetic polymers

Polymer's durability depends on the resistance to environmental factors that cause its degradation: oxygen, moisture, heat and light. It is know that photooxidative degradation causes changes in the polymer properties such as embrittlement, insolubilization, discoloration, changes in wetability, abrasion resistance, loss of transparency and gloss and decrease of mechanical modulus.[55] Therefore to be able to propose appropriate exhibition and storage conditions and also eventual treatment, photodegradation mechanisms occurring in vinyl emulsions have to be studied. To know the degradation system means to be able to determine or, at least suggest, what are the series of chemical steps or reactions involved in the process of initiation and ultimate degradation.[56] Identifying the evolution mechanism is essentially based on the nature of intermediates and final photoproducts.[56]

Polymer photodegradation is photochemically initiated and involves chemical changes that lead to the formation of degradation products, chain scission and cross-linking. Only radiation that is absorbed by a substance may cause a chemical reaction (the Grotthus-Draper law).[57] Absorption of a photon *(hv)* may cause direct breaking (dissociation) of a bond, a process called photolysis and that is generally induced by very short wavelengths (e.g. 254nm). Far more frequently, absorption of near-ultraviolet and visible radiation leads to the excitation of the electrons in the chemical bond, raising them to a higher level of energy.[57, 58] The excited state can be directly involved in the subsequent photochemical reactions. Or, through different pathways it can dissipate that energy (by nonradiative processes eg. dissipation of energy eg. heat transfer; or radiative processes through emission of radiation eg, fluorescence or phosphorescence). If it

passes that energy to another substance creating an excited molecule it leads to what is called photosensitized degradation. [57, 58] Either way the absorbance of the light energy can induce the formation of radicals.[11]

The radicals formed initiate a number of reactions which are independent of light and as substances are exposed to air photooxidative degradation may take place and [59] leads to the development of generally low concentrations of new chemical groups eg. oxidized groups.[56] Another pathway is the reaction of macroradicals with oxygen producing hydroperoxides which are unstable and will break down rapidly to form more free radicals.[37] Some termination reactions cause cross-linking, which creates a brittle polymer network.[59] Several factors influence the degradation pathway of a determined polymer, from its nature to its physical properties. For instance, at temperatures below T_g, the motion of polymer's chains is highly restricted. Under these conditions, when a free radical is generated it may not be able to move very far from the original site (called the cage effect). Increased molecular mobility at temperatures above T_g may induce cross-linking to predominate over chain breaking.

1.2.2. Light absorption

Most of the chemical changes described are photochemically initiated that is they are light induced. Light is by definition the visible range of the electromagnetic spectrum, between 400-700nm.[29] (see Fig. I.8a) Because shorter wavelengths (λ) (<280nm) are absorbed by the atmosphere there is only concern for the ultraviolet (UV) radiation between 280-400nm reaching the earth and being responsible for polymer photodegradation.[29] Quantum energies associated with these wavelengths are of the same order as the energies of some of the chemical bonds present in polymers therefore it would be expected that photodegradation would occur under natural outdoor conditions.(see Fig. I.8 b) [60]

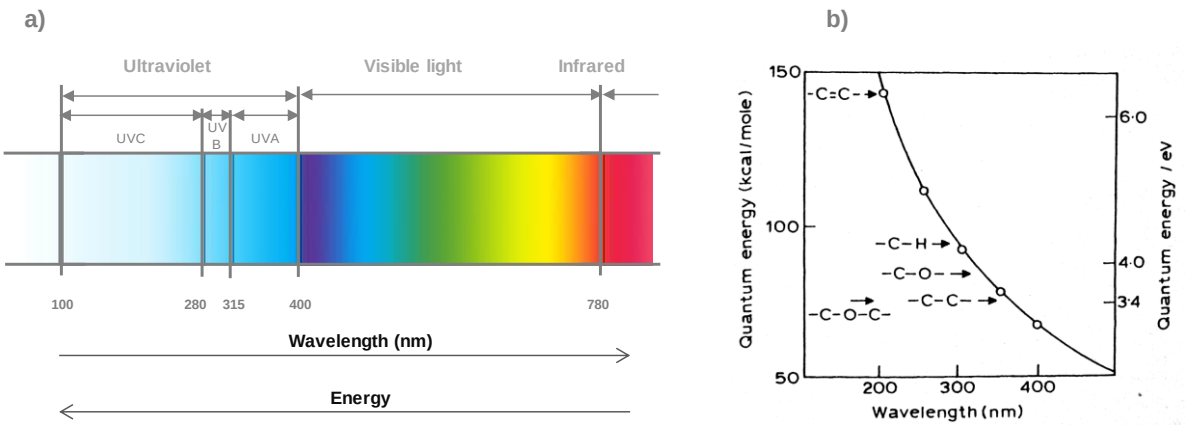


Fig.I.8: a) Electromagnetic spectrum. b) Quantum energies of wavelengths in the ultraviolet region of the electromagnetic spectrum and associated chemical bonds present in polymers.(from [61])

Moreover, commercial polymer structures are more complex than their general molecular formula indicates.[61] They may contain various structural irregularities, branches, external impurities (e.g. conjugated double bonds and hydroperoxide groups) which will absorb light and act as initiation sites for degradation to occur.[61] And as the wavelength of radiation gets shorter and shorter, through the blue and violet region of the visible and into the ultraviolet, the photons possess an increasing amount of energy and are capable of inducing significant photochemical changes.[10] Thus traces of impurities and contaminants and various structural irregularities are often deemed responsible for either being the cause or accentuating the degradation of polymer chains.[61]

In PVAc light absorption can occur directly by the polymer through the carbonyl groups that absorb in the range 300-360nm.[59] The absorbance spectra of two of the homopolymer emulsions studied are shown in Fig I.9. Both unpigmented films of the emulsions show increasing absorptions that starts at visible wavelengths. For the *Vulcano V7* a maximum of absorption starts at c.303nm while for the *Sabu Tempera Acrílica* it starts at higher wavelengths c. 400nm.

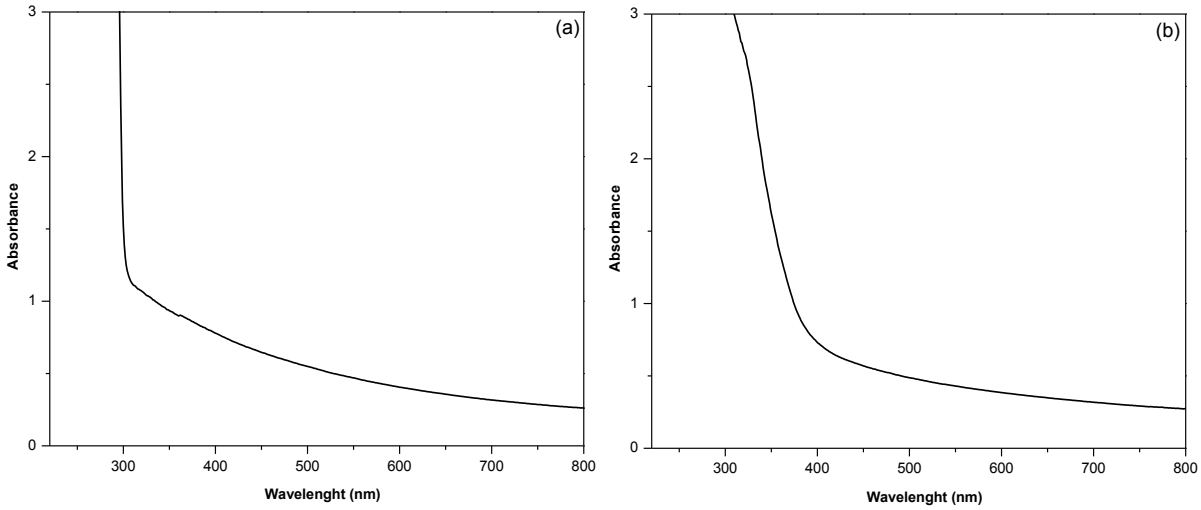


Fig. I.9: Absorbance spectra of homopolymer emulsions (a) *V7* and (b) *Sabu*

1.2.3. Poly(vinyl acetate) photodegradation

David, Borsu and Geuskens studied the photodegradation of PVAc films cast from solution and irradiated with high energy ultraviolet light ($\lambda_{irr} \geq 254$nm) in vacuum and in air.[63-65] Films underwent simultaneous crosslinking and chain scission however both processes decrease when samples are exposed to oxygen.[6, 63] Quantum yields for irradiation in air are 5.01×10^{-3} for chain scission and 2.50×10^{-3} for crosslinking.[63] Yields for chain scission and crosslinking increase with temperature as molecular movements are easier above T_g.[97] Volatile products detected by the authors included acetic acid (CH_3CO_2H), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). Quantum yields of formation of acetic acid under vacuum (1.0×10^{-2}) compared to

[10] $E=hc/\lambda$ where E is the photon's energy, *h* is the Planck's constant, c is the speed of light and λ is the wavelength.

the other products (CO_2:6.5x10^{-3}; CO:6.9 x 10^{-3}) indicate that it is the main product formed during photodegradation.[96]

Buchanan and McGill [66-68] studied the product distribution resulting from the photoloysis carried in vacuum of PVAc films cast from solution. Volatile products detected where similar to the products detected by Geuskens et.al except for the formation of aldehyde (CH_3CHO).[66] Acetic acid formation was the dominant reaction in PVAc photolysis.[68] The irradiated PVAc suffered both chain scission and crosslinking.[67]

Evelyne, et al., studied the photodegradation of poly(vinyl acetate) films cast from solution and irradiated at 254nm.[69] Similar results were obtained as PVAc underwent simultaneous chain scission and cross-linking. The continuous decrease of the carbonyl stretching and methyl bending absorbance demonstrated that side group elimination occurred. Increase of the absorbance at the O-H region was attributed to the formation of hydroxyl and/or hydroperoxide groups. Unsaturation was not detected in the infrared spectra. The authors studied the formation of gel during irradiation and the decrease of molecular weight of the soluble fraction. Simultaneous crosslinking and chain scission was verified.[69]

The proposed mechanisms for the degradation pathway observed with irradiation at 254nm are described as follows. The ester group in PVAc can absorb light forming an excited molecule. Carbonyl groups in the polymer can suffer two types of reaction the Norrish Type I and the Norrish type II. The later has been suggested as the primary reaction occurring in PVAc and accounts for chain scission of the molecules with side group elimination.[68] In an intramolecular process hydrogen is abstracted via formation of six-membered cyclic intermediate product. The resulting products are an unsaturated polymer chain and acetic acid.[59, 68] (Fig. I.10)

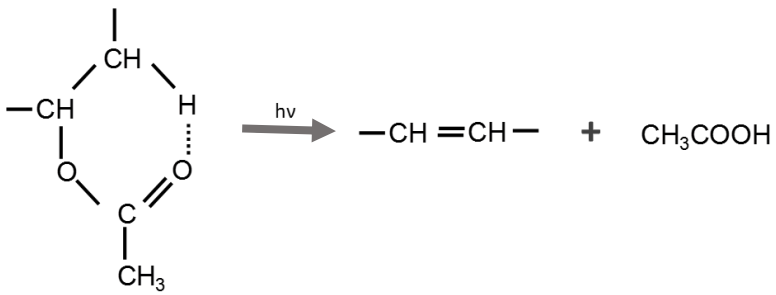


Fig.I.10: Formation of acetic acid through a Norrish type II reaction in poly(vinyl acetate).[59]

Geuskens, Borsu and David rationalized chain scission without side-group elimination by an intermolecular hydrogen abstraction occurring through a seven-member ring transition state instead of a six member ring as in the Norrish Type II reaction (Fig. I.11).[63-64]

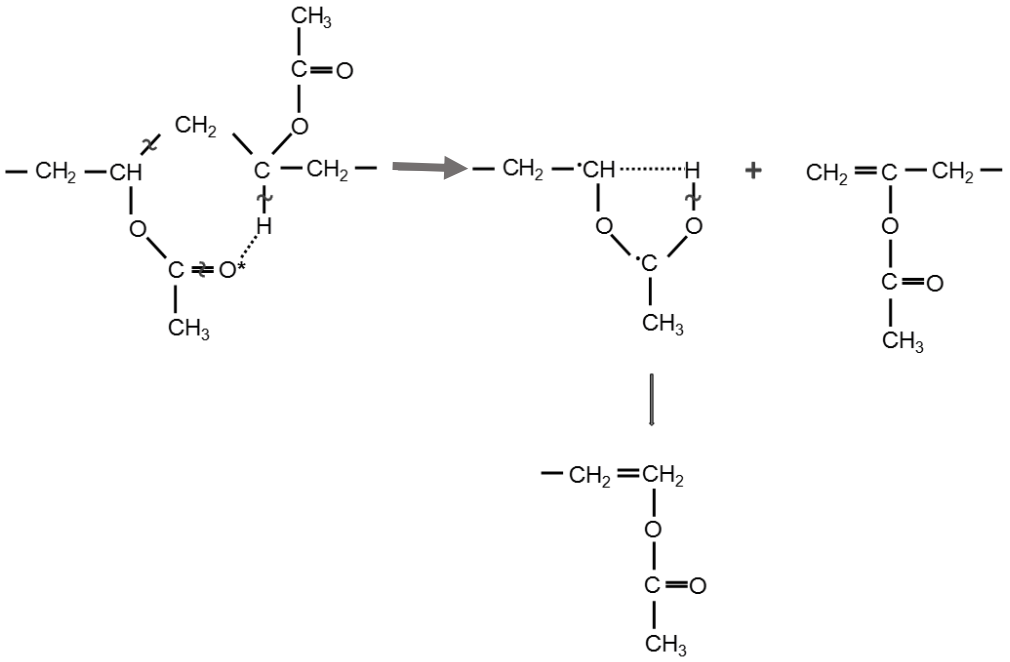


Fig.I.11: Main chain scission in PVAc through formation of a seven-member ring.[63,64]

In the solid state above polymer T_g chain mobility is higher so there is a bigger probability for reaction in Fig.I.11 to occur with a higher yield than reaction in Fig. I.10. In the former case formation of a seven-member ring intermediate is favorable because tertiary hydrogen atoms from one monomeric unit are close to the acetate group of another monomeric unit.[63-64] In fact quantum yields for chain scission and crosslinking (Fig.I.12) increase with temperature.[65] Photodecomposition of PVAc also leads to low molecular products such as CO_2, CO and CH_4 and acetaldehyde. (Fig.I.13)

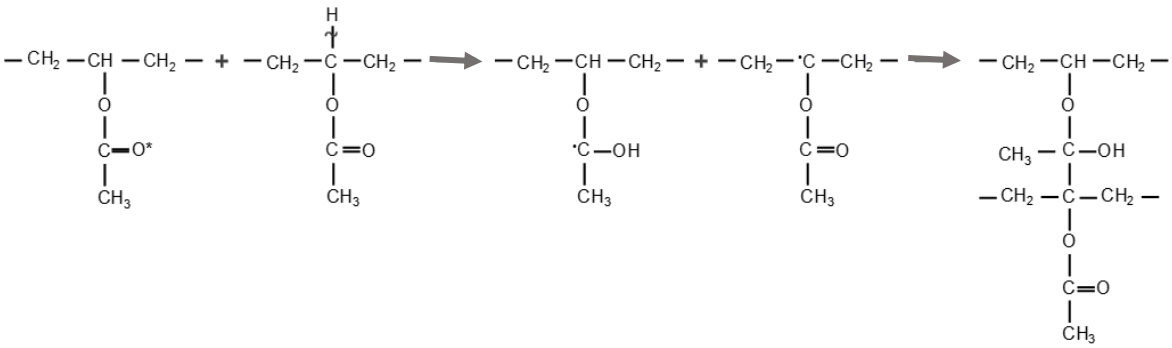


Fig.I.12: Crosslinking mechanism in PVAc as proposed in [63-64]

a) b)

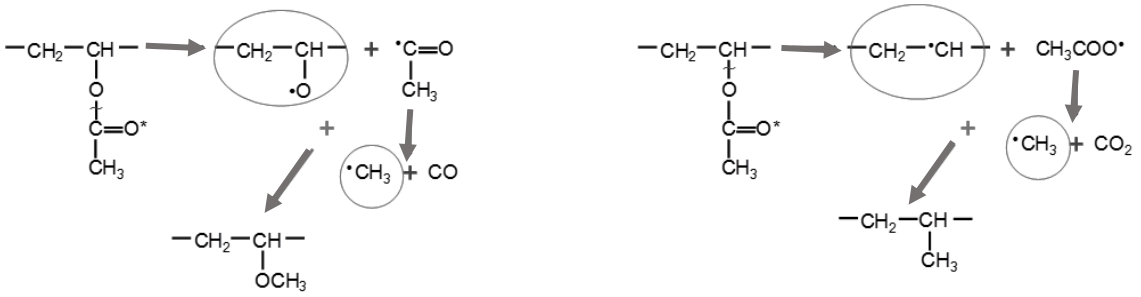


Fig.I.13: Proposed photoinduced reactions in PVAc a) Norrish Type I cleavage leading to decarbonylation; b) formation of radicals with formation of a methyl radical and CO_2. [64, 70]

Photodegradation of polystyrene and poly(vinyl acetate) blends cast from solution and irradiated with polychromatic light (248-578nm) were studied by Kaczmarek.[70] Infrared spectroscopy was used to follow the chemical changes in the pure polymers and in their blends. Changes in the carbonyl group absorbance were interpreted carefully as destruction of the ester groups and formation of new carbonyl groups could be occurring simultaneously. Formation of alcohols, peroxides and carboxylic acids was assessed by appearance of OH/OOH groups absorbing at 3100-3600cm^{-1} [11]. Formation of ketones, aldehydes, esters, acids was followed by broadening and formation of shoulders of C=O at 1500-1800cm^{-1}. Decrease of C=O absorbance from pure PVAc at 1737cm^{-1} and the ester absorbance at 1240cm^{-1} indicated abstraction of side ester groups. Chain degradation was followed through the decrease of the absorbance of CH, CH_2 and CH_3 (2800-3100cm^{-1}). Loss of ester side groups was also observed due to decrease of the methyl bending absorbance band at 1375cm^{-1}. Decrease of C-H from CH_2 absorbance at 2920cm^{-1} was assigned to chain scission and oxidation or crosslinking. The authors concluded that photooxidative degradation of PS/PVAc is more efficient than in the pure polymers. This effect was attributed to the mutual interactions of small degradation fragments or of free radicals that can migrate to the phase of the other polymer and reinitate degradation. When the samples were exposed to emitted light in the range 280-350nm the reactions assessed were the same although they occurred at a different rate and efficiency.[71]

The type of light source (light intensity and wavelength) influences the photoprocesses suffered by polymers.[70-72] Besides, the surface morphology is affected by the solvent used to cast the films and morphology influences the polymer behavior.[73] Also, the presence of additives may affect the degradation of the binder.[74] For that reason, differences between the literature results reviewed so far could be different than results obtained with emulsions and colored artist's paints. Especially when exposed to milder lighting conditions.

[11] Absorptions at approximately 3400cm^{-1} are related to hydrogen bonded peroxide OH; at 3550 cm^{-1} are usually attributed to free hydroperoxides.

In the last years our knowledge regarding the composition, properties and aging behavior of selected artist's vinyl based paints has increased significantly. Within the framework of Conservation research projects have been set and conducted in Portugal and Spain.

Photodegradation of a PVAc homopolymer cast from solution; of a pure homopolymer emulsion (the *Vulcano V7*) and mixtures of both with selected pigments and fillers was studied by Lia et al.. [5, 6] Accurate paint reconstructions of the materials and methods used by the Portuguese artist Joaquim Rodrigo (1912-1997) were created for research. Samples were subjected to light of $\lambda \geq 300nm$, during 3500h and 5000h with a constant irradiation of $800W/m^2$ supplied by a Xenon-arc lamp. Results show that this PVAc waterborne emulsion and its paints undergo loss of plasticizer and that chain scission is the main degradation pathway and no side group elimination was detected. No molecular evidence was obtained for the formation of other carbonyl functions, the disappearance of the carbonyl group or the formation of hydroperoxides. The sensitizing effect of some pigments/fillers ($CaCO_3$ and ultramarine) and the protective effect of others (red iron oxide and titanium dioxide) on the degradation level of PVAc emulsion paint films was also shown. The authors reason that the protective effect of the later can be explained because these pigments absorb radiation below 400nm competing for light with the polymer. The sensitizing effect exhibited by the calcium carbonate is probably due to the intensifying effect of the light absorbtion by the polymer induced by the filler. A similar process can be attribute to the ultramarine as this is mixed with kaolin. The analysis of naturally aged samples taken from Rodrigo's paintings (works created in the 60, 80 and 90's) also showed that the binding medium used by the artist is in good preservation conditions as the infrared analyzes conducted showed only the loss of the plasticizer.[5,6]

Doménech et al. subjected the *Flashe* commercial artist's PVAc based paints (Oriental red, Green armour, Senegal yellow and Burnt Sienna) to artificial ageing.[31] After natural drying during one year the paint samples were aged artificially by exposure to a Xenon arc light. The following conditions were used $1.1W/m^2$ in the visible range at 420nm and $56\ W/m^2$ at 300-400nm. Ageing tests of 400h and of 800h were performed. No significant migration of additives was detected in film's surface after 800 hours of ageing but, the disappearance of a PEO-type surfactant from the bulk of the paints was detected. Several chemical changes were identified. Appearance of new carbonyl groups revealed by broadening of the original ester absorbance band. Namely the growth of a shoulder at $1718cm^{-1}$ was ascribed by the authors to free acetic acid. Decrease of the CH_3 stretching absorbance indicates that side-chain reactions took place. Chain scission was also detected. These changes and the loss of additives were correlated with increased stiffness of the irradiated commercial PVAc paints.[32]

S.Wei et al. exposed some of the *Golden* vinyl paints (commercial paints dissolved in ethanol and pigmented with burnt umber, cobalt blue, cadmium red dark, nickel azo yellow and titanium white) produced by *Kremer* to accelerated ageing.[75] A $910W/m^2$ Xenon arc source of light equipped with a filter to provide radiation between 295-800nm was used for this purpose. Samples were exposed to these conditions during sixty days. Loss of ester groups leading to formation of acetic acid during ageing was quantified by pyrolysis–gas chromatography/mass spectrometry (Py–

GC/MS). Although both unaged and aged samples show the presence of acetic acid, in the aged samples the quantity of acetic acid is higher. The infrared spectra of the aged samples did not reveal any noticeable changes. The authors argue that the formation of C=C double bands, formed when the Norrish type II mechanism is involved in the acetic acid formation, must be in a low amount and therefore not detectable in the infrared spectrum. The authors also suggested that formation of new oxidation products might counterweigh for PVAc deacetylation and therefore no significant changes in the carbonyl absorption would be distinguished. Loss of the diethyl phthalate (DEP) plasticizer during ageing was also established.

Toja et al. studied the influence of different DBP concentrations (10, 20 and 30%) on the photodegradation of PVAc films casted from solution.[74] Samples were aged with exposure to a xenon arc lamp with a cut-off filter at $\lambda<290$nm. Irradiation was kept constant at 765W/m^2. Samples exposed to ageing times from to 100 and 2000h were studied. After photooxidative ageing samples that did not contain the phthalate showed loss of initially C=C bonds present in the polymer backbone. Moreover, the intensity of the bands related to the acetate side chain did not show any changes in the infrared spectra. However, differences were detectable in the samples containing DBP. Obviously some are due to the progressive loss of the phthalate. Yet the results suggest that loss of the PVAc ester group is promoted by the phthalate. Deacetylation of the polymer was followed by the slight reduction of the asymmetric stretching of the acetate group at c. 1434cm^{-1}. Formation of oxidation products was detected by the slight increase of the OH stretching absorption bands.[74]

1.2.4. Poly(vinyl chloride) photodegradation

PVC photodegradation mechanisms were studied systematically and in detail by Decker and Balandier.[45,46] The main results were summarized in [47], including the reaction quantum yields for the production of HCl (15x10^{-3}), carbonyl and peroxide groups (5 x10^{-3}, 3 x10^{-3}) as well as chain scission (2.6x10^{-3}) and cross-linking (0.6x10^{-3}) for irradiation $\lambda>250$nm, of films in the presence of O_2. The authors also measured reaction quantum yields in the presence of N_2 and in solution. The main conclusions of these works are summarized in Fig. III.14, in which absorption of light by the polymer matrix results in the production of Cl radical (Cl·) that may: *i)* react in a cage reaction leading to the formation of an additional conjugated double bond and HCl, ("zip" dehydrochlorination) or *ii)* react with another polymer chain for the formation of HCl and a new macroradical. The macroradical may undergo "zip" dehydrochlorination with the formation of new polyenes, chain scission or react with O_2 for the production of a hydroperoxide; by light absorption it will further photooxidize, leading to the well know formation of ketones and other oxygenated functions. The authors also conclude that the presence of O_2 does not quench the radical chain reaction but further promotes the formation of macroradicals, which will react by releasing Cl· that in turn will catalyze the "zip" reaction. It is worth mentioning that it is stated that "In any case, whatever the nature of the chromophore that initially absorbs UV light in the original material, polyene structures that accumulate in photolysed PVC will rapidly become the predominant

absorbing chromophore, because of their large extinction coefficients: ε=42,000 $Lmol^{-1}cm^{-1}$ for trienes and 210,000 $Lmol^{-1}cm^{-1}$ for octaenes". [47]

Lemaire and Gardette have further contributed to the understanding of the photooxidation pathways, namely by proposing the main oxidation photoproducts: carboxylic acids, chlorinated ketones and acid chlorides, in this order [72]. The main intermediate found was the hydroperoxide depicted in Fig.I.15.

Both research groups concluded that the "zip" dehydrochlorination reaction, Eq. 2 and 3 in Fig.I.14, was the main photodegradation pathway when irradiation of PVC films was carried out at λ>290 nm in the presence of O_2 or N_2. This reaction leads to an increase in the polyene chain length which is responsible for the extensive yellowing observed in PVC photodegradation.

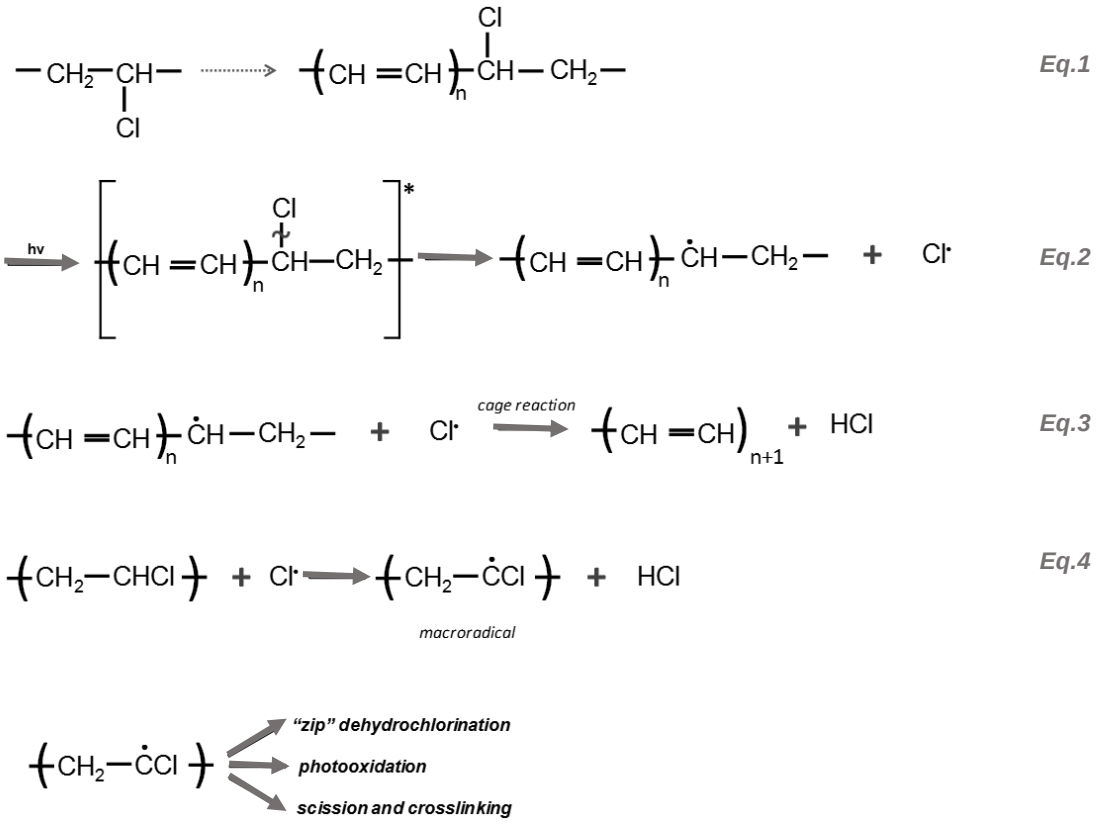


Fig. I.14: Proposed photodegradation mechanism for PVC

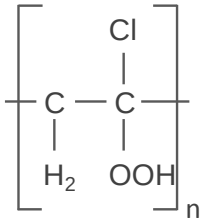


Fig.I.15 – Hydroperoxide formed during PVC photodegradation.

The effect of photo-active pigments such as TiO_2 and ZnO was also studied by Lemaire and Gardette [44]. No photocatalytic effect was observed in the photo-oxidation of poly(vinyl chloride), for irradiation at λ>300 nm, as both pigments presented a screening effect by efficiently competing with the polymer for light absorption.

According to Kaczmarek et al. PVAc and PVC blends undergo degradation when irradiated at 254nm. The photooxidation products developed included alcohols, peroxides and carboxylic acids and new C=O functional groups like ketones, aldehydes, esters and acids. Abstraction of side ester groups occurred in the PVAc while chloride atoms abstraction took place in the PVC. Chain degradation and crosslinking was also detected. Foremost PVAc was found to decelerate the photooxidative degradation of PVC.[73]

Taking into account that in ethylene-vinyl acetate copolymers the properties are determined by the VAc content [76] a significant influence of the ethylene fraction in the terpolymer studied was not expected.

Based on what was described for the photodegradation of PVC, it was expected that the P(VAc-E-VC) formulation *Vinamul 3469* would not perform as well as the homopolymer based *V7*.

1.2.5. Additives and plasticizer migration

A number of additives such as surfactants and plasticizers have limited solubility in the polymers, which cause them to migrate to the surface.[33] Phthalates are not chemically bond to the polymer, but remain as a freely mobile and leachable phase that can be lost from the film over time.[77] Diffusion of these molecules through the polymer depends on additive chain size and shape as well as on the polymer free-volume, which is connected to its chain mobility.[78] The process is not straightforward and depends on other factors. For instance, additives with similar masses and of different shapes can behave differently. At low temperatures molecules with longer linear chains can diffuse slower than a spherical one of similar molecular mass; however, at higher temperatures the order is reversed.[78] Branched plasticizers are more permanent than the equivalent linear plasticizers because, branching hinders the plasticizer movement and may facilitate entanglement between the plasticizer and the polymer matrix. Migration, and removal by volatilization and extraction is therefore more difficult.[78]

Although phthalates are relatively non-volatile at ambient temperatures [24] (measured values for DBP are $1,2^{-4}$ to $2,5^{-4}$mmHg at 25ºC and for DiBP $1,8^{-6}$ to $5,8^{-4}$mmHg at 25ºC [22]) decrease of their content from emulsion and paint samples has been reported. Loss of diethyl and dibutyl phthalates from commercial PVAc artist's paints has been reported after artificially ageing with UV light and thermal ageing.[79] The same research group quantified plasticizer loss from pure PVAc films cast from solution under UV light.[39] The results showed that different plasticizers behave differently. DBP decreases significantly while diethyl phthalate remains fairly constant during ageing despite its lower molecular weight. The same process and results were observed in colored artist's waterborne paints by Silva et al.[17] Toja et al. found similar results DBP disappeared progressively from PVAc films under thermo and photo-oxidative ageing.[74] Tendency for additive segregation and deposition in polymer surfaces and interfaces is a commonly know disadvantage of synthetic paints and a common outcome in aging of acrylic waterborne pigmented and unpigmented paints.[80,81] However in some cases deposition may not occur. Light ageing of acrylic TiO_2 paints resulted in the disappearance of the surfactant that accumulated in the air film interface due to its photooxidation.[82]

1.2.6. Discoloration (yellowing)

Generally speaking yellowing of polymers implies that chromophore groups are being formed as these are responsible for UV absorption that extends into the visible (400-800nm). In polymers these groups are polymer chains that have conjugated double bonds. Formation of these unsatured groups (–CH=CH–) is attributed to photo-oxidative degradation.[59] Polyene structures concentrate in a superficial layer and as they strongly absorb the entire incident light, this layer can act as an efficient ultraviolet screen that should prevent the underlying layers from being further degraded.[46, 59]

Reports on yellowing of emulsion films can be found spread in the published literature. Acrylic dispersions exposed to light and thermal aging have displayed discoloration although the authors did not attribute the phenomenon to any reaction in particular.[83] Thin films of n-butyl acrylate-co-methyl methacrylate copolymer, p(BA-MMA), exposed to simulated indoor sunlight (visible spectrum with reduced intensity below 400nm) showed a sharp increase in yellowing in the first few hours of exposure (equivalent to 16 years of natural exposure) that was bleached with further illumination.[81] Yellowing of an acrylic binding medium during natural aging in the dark has been reported by Whitmore and Colaluca.[84] The discoloration was attributed to the formation of conjugated polyene structures and accounts for acrylic films to fluoresce under ultraviolet illumination.[12] [84]

A long term natural ageing study was been conducted by Jane L. Down at the Canadian Conservation Institute.[85] Measurements of yellowing after c.11-12 years of light ageing and c.13-14 years of dark ageing showed that in 25 PVAc homopolymers and copolymers adhesives, yellowing occurred more quickly during light exposure than in the dark. Poly(vinyl acetate) adhesives subjected to dark aging showed a degree of yellowing between 0.0277 and 0.0970. Adhesives subjected to light aging showed a degree of yellowing between 0.0389 and 0.1975.[13]

Several PVAc based dispersions have been found to yellow under thermal, dark and sunlight aging although discoloration was less severe in the later case.[86] The study showed that color was the most widely and significantly changed physical property in the dispersions tested. Because other properties of the studied dispersions did not change significantly the authors concluded that yellowing of the samples should be related to additives.[86]

1.2.7.Manufacturing and additive content

Manufaturing and processing parameters of sytnthetic emulsion paints have found to have an affect over the paint's degradation mechanism. In addition to a more immediate influence in the paint's properties (e.g. physical characteristics like T_g or film morphology) the role of these

[12] If a molecule absorbs light energy to form an excited state and losses that energy by emitting radiation in a longer wavelength the process is called luminescence.[11] Fluorescence appears mostly in molecules with conjugated systems of double bonds and rigid structure, such structure shifts the absorption and emission wavelengths into the visible region.[57]

[13] The degree of yellowing A as a function of time was calculated as $A_t=[(Abs_{380nm} — Abs_{600nm}) \times 0,1mm/film\ thickness]$.[85]

additives in the degradation of the paint was been stressed by several authors. A study conducted by Allen and Regan on acrylic waterborne paints has showed an interrelation between their photoxidative degradation and the presence and nature of impurities and oxidation products generated during emulsion manufacture.[87] The authors investigated the effect of additional comonomers, surfactant types and initiator systems used in emulsion polymerization on the ageing of a p(BA-MMA) based emulsion exposed to $\lambda<300$nm. Results showed that hydroperoxides are formed during the polymerization of the emulsion and their high concentrations are associated with the presence of residual initiator (a persulphate in this case). Moreover, hydroperoxide concentration rises with the use of anionic and non-ionic surfactant systems.[87]

More importantly, as has been mentioned a recent studied conducted by Toja et al. showed that during photo-oxidative ageing of PVAc the plasticizer dibutyl phthalate slightly increased the degradation of the polymer.[74]

1.3. The case of Julião Sarmento's paintings

Born in Lisbon in November 4th of 1948 Julião Sarmento lives and works in Estoril. He is one of the most successful contemporary Portuguese artists and has achieved international recognition. Working since 1974 Sarmento has created with painting, film, video, sound, sculpture, installation and multimedia. Julião is part of a group of artists that in the end of the sixties was interested in exploring the potentialities of synthetic paints. At the time there was an urge for creative confrontation with what was being produced outside of Portugal [88] and Sarmento was seeking to create newer aesthetic effects. Besides Julião was interested in synthetic paints due to its symbolic meaning. Using them meant a cut off with traditions. In technical terms Julião quickly realized the benefits of these new paints, from their non-toxicity to their quick drying and from over approximately 35 years of artistic practice made use of a broad range of PVAc products from ready to use artist's paints, to homemade paints, to industrial products. Sarmento's wide use of vinyl based paints made his work particularly important to be studied. Furthermore Sarmento's works were chosen due to conservation concerns (discoloration) present in a significant number of his paintings created in the 90's.

II. Julião Sarmento a Portuguese artist from the 21st century: Results on his materials and methods

2.1.Secrets of the craft

The research here described included a close collaboration with the artist. As analyzes performed on several paintings provided information they also arouse several questions that the artist was able to clarify. Several interviews, short conversations and also a workshop lectured by Sarmento (Fig. II.1) for master students of Conservation and Restoration attending the lectures of History and Techniques of Artistic Production were used as first-hand invaluable sources regarding the materials and techniques used and reasons behind the artist choices.(see Appendix Ia and Ib: Interviews with Julião Sarmento)

Fig. II.1: Julião Sarmento at work during the workshop held at the Departamento de Conservação e Restauro-Faculdade de Ciências e Tecnologia/Universidade Nova de Lisboa, 3rd of May of 2010.

2.2. Academic/practical training

Julião studied Painting and Architecture at the Escola Superior de Belas Artes in Lisbon, from 1967 through 1974. Although both Portuguese artists and artist's paint manufacturers were keenly aware of the development in the artist's materials international scene, it was not easy for Portuguese young artists studying at the fine arts school to explore that progress. As Sarmento reveals, use of new materials was not allowed and students were forbidden to use acrylic paints. Julião stated that the school "really looked like a XIX century school". However, that prohibition did not stop him and Fernando Calhau (Portugal, 1948-2002), his colleague at the painting course,

from exploring synthetic paints. As Fernando Calhau says: “I remember putting, with Julião Sarmento, canvas to dry at the sun in the school-yard. We could paint more rapidly than our colleagues”.[89]

Albeit his problems with school rules Sarmento admits that his academic experience may have had some influence in his working methods, especially in one of the most important features of the artist’s working method: the manual manufacture of his paints. His training included the apprenticeship of traditional methods, so the students were taught to mix the dry pigment with the binding medium. In the artist’s own words: "...we had to use oil paints, egg temperas made by us, which is funny making our own paints...maybe that is why I later started to do my own paints.”. Joaquim Rodrigo, for whom Sarmento worked as an assistant in 1969, may too had an influence since Rodrigo also made his paints by mixing the *V7* white glue with dry pigments.[5] When questioned about the technique resemblance between the two artists Julião says that: “...he didn’t teach me [to do my own paints] it was me working there. I saw things were much cheaper and that was what mattered to me. It was really a question of economy.”.

2.3. So why synthetic paints?

The main reason for Julião’s interest in synthetic paints it is because they represented a style innovation and rejection of tradition. Synthetic paints were symbolic, they represented what was new. Being a “son of the *pop culture*”, it is not surprising that in 1968 he tried acrylic paints “because those were the paints that the American and English *pop* artists of that time were working with. And they were our heroes!”. He just had to use the materials of the XX century artists. Convergence between the aesthetic features the artists were seeking to achieve and the practical properties of the synthetic paints is clearly described by Fernando Calhau: “The acrylic paints have high hiding power and they produce flat and uniform surfaces much more easily than with oil. Therefore, there was a working style that was affected by the material and that was decisive in our evolution, in our autonomy in relation to the School, and in our relation to the Pop and the *minimal*…the quality of the material [acrylic paints] compelled you to a certain working speed.”.[89]

Sarmento’s rejection of traditional paints was also based on technical grounds. The long drying time of oil was not compatible with his quick and immediate working methods. The artist explains very plainly how a traditional medium could not fit his aims: “Imagine what is like to do a six meters square area, mixing various substances, in oil. It would take months, years to dry, it would probably cost a fortune and I wouldn’t get the kind of surface I want.”. (Fig. II.2) The only disadvantage mentioned by the artist was the paint’s tendency to form surfaces that were not very glossy.

Because Sarmento liked to work with new and unknown materials he did not worry to gather information regarding the new paint’s characteristics and durability. The artist admits that he gives privilege to the material’s visual quality over their durability. In his own words: “If the works disappear, they disappear....I will not modify one inch of my work thinking about durability....The works get old. They get the look of time passing by which is also important.”.

Fig. II.2: Canvas prepared to receive drawings at Sarmento's studio located at the Centro Empresarial in Sintra-Estoril in 12th of January of 2004.

2.4. Review of Julião Sarmento's materials and techniques

The differences found in Julião's work are mostly related to the formal nature of his means of expression. The ideas, wishes and obsessions are permanent and are a mirror of his interests, where cinema and literature are favored without putting aside inspiration coming from everything he encounters of all that can catch his most important sense, his eyes.[90] Technique (in a broader sense) is just a way of using as quickly as possible the things that are at the artist's disposal to represent his idea.[90]

a) 1962-1969: household paints on hardwood

Between 1962-69 Julião used mainly hardwood reinforced with a pine cradle as a painting support. A commercial household paint was used to create dull or mat areas. Since this paint was somewhat transparent Sarmento preferred *Robiallac*[14] household paint to create brighter areas. Also painted in the end of the 60's were two or, three works in which the artist preferred to use commercial artist's oil paint. There should only be a few examples from this period because unfortunately Sarmento's work from this period was lost at the Chiado fire.[15]

b) 1969-1974: acrylic on canvas

[14] *Robbialac* is a Portuguese paint manufacturer. It was established in 1931 and nowadays is registered as *Tintas Robbialac, S.A*. It was the first company to introduce household PVAc aqueous emulsion based paints in Portugal under the trade name *REP* (Robbialac Emulsion Paint). This series of PVAc based paints have been produced at least since 1954.[5]

[15] The fire occurred at 25th of Augusto of 1988, in Lisbon downtown namely in the Chiado area. This is an important heritage area due to its architecture heritage and offer in tourism activities. Besides the loss of commercial stores and offices there was loss of several buildings from the XVIII.

Later he prefers pre-prepared linen canvases bought either in *Casa Varela* or at *Corbel*.[16] A layer or two of acrylic gypsum[17] was frequently applied by the artist on top of the commercial ground layer that came on top pf the canvas. Both Julião and Fernando Calhau wished to use the *Aquatec* acrylic paints, used by American artists and advertised in international art magazines of that time. As they could not find them in Portugal they chose to use *Talens* paints.

c) 1974-1981: Painting is discarded

For Sarmento art is a form of language. Now and then when a certain creative expression is worn-out, things are too predictable and tedious they give way to the need to look for new means to present the same speech.[90,91] In the mid 70's Sarmento shifted to what he designates as "reproducible materials": photography, cinema, video, sound, installations and performance. Painting was completely abandoned and for seven years he did not paint or draw, except as a tool to plan other works such as installations for example.

d) 1981-1986: *Sabu* paints over paper

Only in the 80's when painting was revitalized internationally did Sarmento go back to painting.[92] Works from the first half of that decade are characterized by raw and bold brushstrokes; by strong colors and contrasts; by a complex and heterogeneous set of fragmented or superimposed imagery, scenes or elements.[91] The same work encloses words and images of different nature, figurative or abstract, realistic or geometrical; of different scales, from a macro to a general view; of different depiction strategies from the simple sketch to the thorough drawing.[90] Forms are defined by the artist's brushstroke and Sarmento describes it as drawing with paint.[91] An example of this complex expression can be found in *Cinquenta dois (Dez quadros para o ano 2000)* painted in 1985, Fig.II.3.

Sarmento starts to use *Sabu* paints and paper as the usual support. Even if his choices follow the artistic trend of the 80's, valuing the artist gesture, the taste for the pigment and the materials, at the same time the criteria for selecting a particular kind of material is an economic one: "...by that time my attitude was very experimental regarding the materials...I got a 'kick' from trying new materials but, I also used materials at hand and that were easy to get, that were cheap, because I couldn't spend the same money I can now.". This attitude has guided him throughout his career because, it became natural to do so. During these four years Sarmento only worked with paper, a brown-grayish grocery paper. This crude paper usually used to make grocery parcels has been the subject of several interpretations. They are "…old papers recovered by the whimsy of a secret reason."[90] being the "secret reason" in the artist's own words the lack of financial conditions to acquire any other kind of support. Reams of this paper could be bought for the price of a piece of high quality drawing paper and to obtain bigger formats several pieces could be juxtaposed.

Because *Sabu* was labeled as an "Acrylic Tempera" it is usual to find works from this period described as "acrylic on paper". Sarmento described the *Sabu* paints of that time as being "sort of

[16] *Corbe*l is another Portuguese fine arts materials store, situated in downtown Lisbon. It was founded in January of 1917.

[17] White gesso primer is a product sold as suitable for priming surfaces prior to painting. The name is misleading as FTIR results showed the white color is given by calcium carbonate. This seems to have been a tendency as the first producers of acrylic primers (*Liquitex* and *Bocour*) gave the name gesso to their acrylic grounds in the 50's although its composition is not the same as in a traditional gesso ground layer.[93]

an acrylic" that had a "big yield", one could dilute them and still obtain a colorful paint. Julião also remembers having to deal with the problem of manufacturers changing paint formulations without notice. Different bottles with the same reference and with the same color could present different characteristics for instance in terms of paint consistency.

The artist is attentive that paintings from this period do not show visible signs of degradation: "Curiously materials that were told that would only last a month or, two months…I would work with brown grocery paper which is a highly acidic paper and the *Sabu* paints that were considered to be low quality paints. Yet the works look like were made today when they were done in 1980". Still, precaution in the application should be taken as Sarmento recalls that thicker layers of concentrated *Sabu* paint could develop cracks. An important aspect of paintings from this period is paper deformation as the support reacted to the water contained in the emulsion paint.

Fig. II.3: *Cinquenta dois (Dez quadros para o ano 2000),* 1985-86. 135x200cm. Poly(vinyl acetate) on paper. Museu Colecção Berardo.

Fig. II.4: *Salto*, 1985-86.200x260cm. Poly(vinyl acetate) over paper. Museu Colecção Berardo.

e) 1986-1990: *V7* + dry pigment

Later Julião opts definitively for textile supports and homemade paints. This way the materials would be cheaper and effects difficult to achieve with other kind of paints could be obtained. Selective handling of the ratio and mixture of binder and dry pigments allowed him to explore different aesthetic effects. Paintings with huge dimensions could be created by taking advantage of the drying speed of the white emulsion glue. The works are characterized by highly textured backgrounds that recreate tensions and are well adjusted to receive a diverse imaginary.[90] Frequently the works are composed of more than one canvas of individual but interrelated images, since they have meaning not only in the larger unity of composition but also as separate entities.[92] The materials are usually the *Vulcano V7* white glue and colour is obtained with the *Cenógrafa* dry pigments, both produced by *Favrel*. The working methods are experimental and spontaneous.

Julião Sarmento explained that the kind of pigments used has little importance to him, he uses "what they put in the *Cenógrafa* pigments". The limited range of colors of this brand fits perfectly within the artist's attitude towards color. The absence of a varied *palette* of colors is "only for a matter of choice, they [the colours] don't interest me, I think they distract from the essential questions. You start looking at the yellows, at the pinks, etc., which are important to some people but not for me…the colors they have solve my problems…that doesn't mean that I don't

manipulate the colors. If I want to change them I will.". Recycling paint residues by mixing them together was another method employed to widen the range of colours. Plus Sarmento also manipulated the colours by adding other colouring substances like organic synthetic pigments.

Creating "palpable" surfaces by mixing various kinds of materials to the paints became usual. Searching for tangible surfaces Julião strategically added to the vinyl glue earth, sand, tobacco, matches, and paper and so on. By simply mixing poorly the pigments a rough painting surface would be put in to evidence. Examples of the use of earth/dirt as pigment are *Just a Skin Affair* from 1988 (Fig. II.5) [19,94] and *Dez Anos*, 1986/1996. In the first case Sarmento simply swept the artist's studio and mixed the gathered soil with the *V7* white glue.[19,94] On the second case a refined pigment was used. Dust that had accumulated for ten years (hence probably the painting's name *Ten Years*) in the studio's floor was sifted into a fine brown powder. This was mixed with the white glue as a pigment to produce a brownish coloured paint. Earth was extensively used as an artistic material by Sarmento. Further on it will be seen that it could be used as a pigment or, simply spattered around the surface to create spots of colour over white backgrounds.

Fig. II.5: *Just a skin affair*, 1988. 130x141cm. Poly(vinyl acetate) on canvas.
Centro de Arte Moderna – Fundação Calouste Gulbenkian.

Wanting to do "really big paintings" Julião works with 2,15m wide rolls of cotton duck canvas. No size or ground layer is applied. The textile is not washed before use and is simply wetted immediately before paint application. Wetting the support helped because the wet textile would

stick to the protection plastic covering the floor and the paint was more easily spread over it. The paint could be prepared previously in buckets or by mixing the binder and pigment directly on top of the wetted support.(See Appendix I, Interviews with Julião Sarmento for a more thorough description of the painting method). After drying and the motives painted or drawn the painting would be stapled to custom made stretchers.

f) 1990-2004: *V7* + white and black dry pigments

When Samento started the commonly called *White Paintings* series in the beginning of the 90's, the plastic expression of the paintings was simplified and so were his materials. Over white backgrounds, fragmentary human figures performing ambiguous gestures are sketched in black. These figures are depicted faceless since Sarmento was interested in finding a general representation of women: "if you draw eyes, a nose, a mouth then you have a portrait."[95] Colors were reduced to black and white or to grey resulting from the mixture of both. The monochromatic aspect of the background is broken by its uneven topography: by differences in thickness and use of highly textured areas. Case studies from this period are: *Pintura Cega (três instrumentos de prazer e um de dor)* (1990)*; Wasting my time with you* (1991), *I don´t want to go to sleep* (1991), *Frozen Leopard* (1991-92), *Belém* (1992) and *An Involved Story* (1998). (Figs. II.6-13)

These works are characterized by a quest of depuration and sobriety.[91] However as this research has disclosed this simplicity is only apparent. The preparation of the paint involved the artist's knowledge and control over several technical advantages offered by the emulsion binder. That allowed him to explore a rich variety of textural effects on this white backgrounds.

Choice of color for these paintings is a conceptual one. It is directly connected with the cultural context in which they are created. General understanding is that the name for this series derives from the white background. However, Sarmento explained that the designation was given by him because in Occidental civilization white color is usually seen as a symbol for neutrality.[88] In order to achieve neutrality Julião has to work with the right color and that is not necessarily white. For example, in 1992 while working in the Amazon in Brazil a light green was the color chosen to render the paintings background color. In the same perspective Sarmento explains how while "working in Marrakech, I had to adapt and to achieve the necessary neutrality, I had to work with the right colour...".[88] Therefore in *Laura and Alice (14)* a work made in 1994 a red pigment bought in Marrakech was used.

Paints from this period are homemade and materials are narrowed to the *Vulcano V7* as the binding medium and to white and black *Cenógrafa*dry pigments. Moreover, dirt or soil spattered in the surface completed this *frugal* choice of colours. Aware of the expressive potential of both, Sarmento exploited them in a variety of ways, such as changing the ratio between binder and pigment to create differences in surface, ranging from glossy to matte and from smooth to granular. The artist's description of the method is quite explicit: "For example, if you have a portion of PVAc and a portion of titanium white[18] you have numerous ways to obtain a different surface appearance after drying, it can be shiny, matt, very smooth or, very irregular. It depends on the

[18] Although Sarmento described is working methods refering to the use of titanium white what he was in fact using was lithopone. He always thought that the pigment used in the *Cenógrafa* brand was the TiO_2.

amount of water you add, it depends on the way it is mixed (if you mix it unevenly or thoroughly). Using the same amount of pigment and binder you can get a very different result. Then if you vary the ratios the outcome is endless." For these paintings the usual ratio would be 1Kg of *Cenógrafa* dry pigment for 5L of *Vulcano V7*.

Drawing remains essential even more when a traditional material like graphite is chosen.[91] While this is used over white backgrounds, chalk is used over black backgrounds. The graphite drawings were initially protected with commercial hair spray but as the paintings "kept that smell of hairdressers" Sarmento started to use artist's fixative from *Talens* or *Winsor & Newton*. Drawings were made with soft graphite sticks and along the outlines it is frequent to see traces of the nearby lines. That happens because while drawing Sarmento did not worry about his hand catching the graphite powder and contaminating adjacent areas. It is also frequent to see drawing lines that do not form coherent figures or, seem to be outsiders to the composition. That is an explicit strategy to leave uncovered "failed attempts".[91] In both cases the artist assumes it as being part of the creative process.

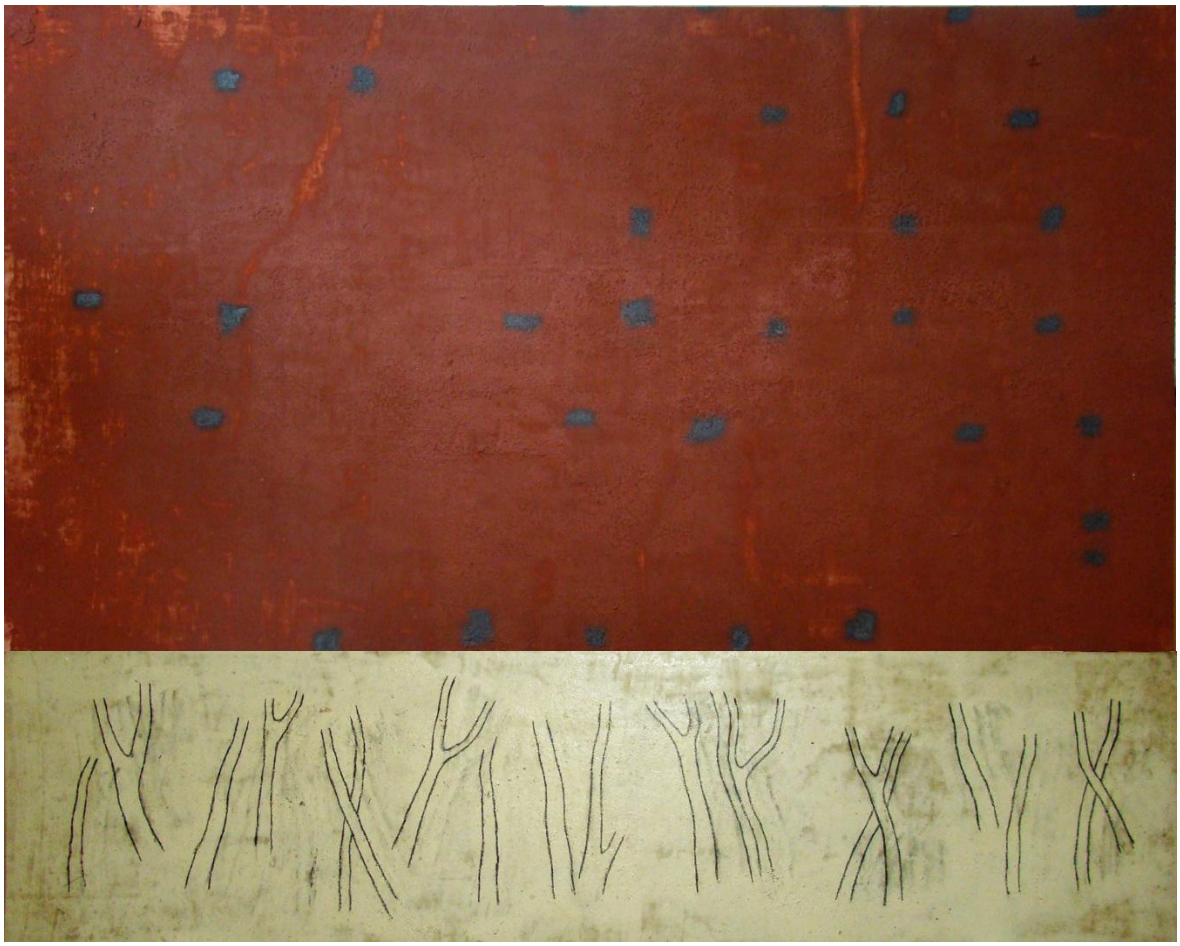


Fig. II.6.: *Frozen Leopard,* 1991-92. 275x315cm. Poly(vinyl acetate) and graphite over canvas. Centro de Arte Moderna – Fundação Calouste Gulbenkian.

Paint is applied following the same sequence described for paintings from the 80's: wetting the canvas, spreading it on the floor, applying the paint and finally letting it dry. Paint was prepared in buckets and binder and pigment would be mixed with an industrial blender. After achieving the

desired consistency Sarmento would spread it over the previously wetted support. To create additional surface irregularities drops of water would be dribbled on top of the fresh paint forming craters (that is the case of *An Involved Story*). Because sometimes the background would look too white Julião would mix soil (or any other substance) with water. By speckling the mixture over the surface, brownish craters and stains were left over it. The painting might be temporarily stapled to the wall and then the artist would proceed with the drawing. Stretching the canvas would be the last step of the process.

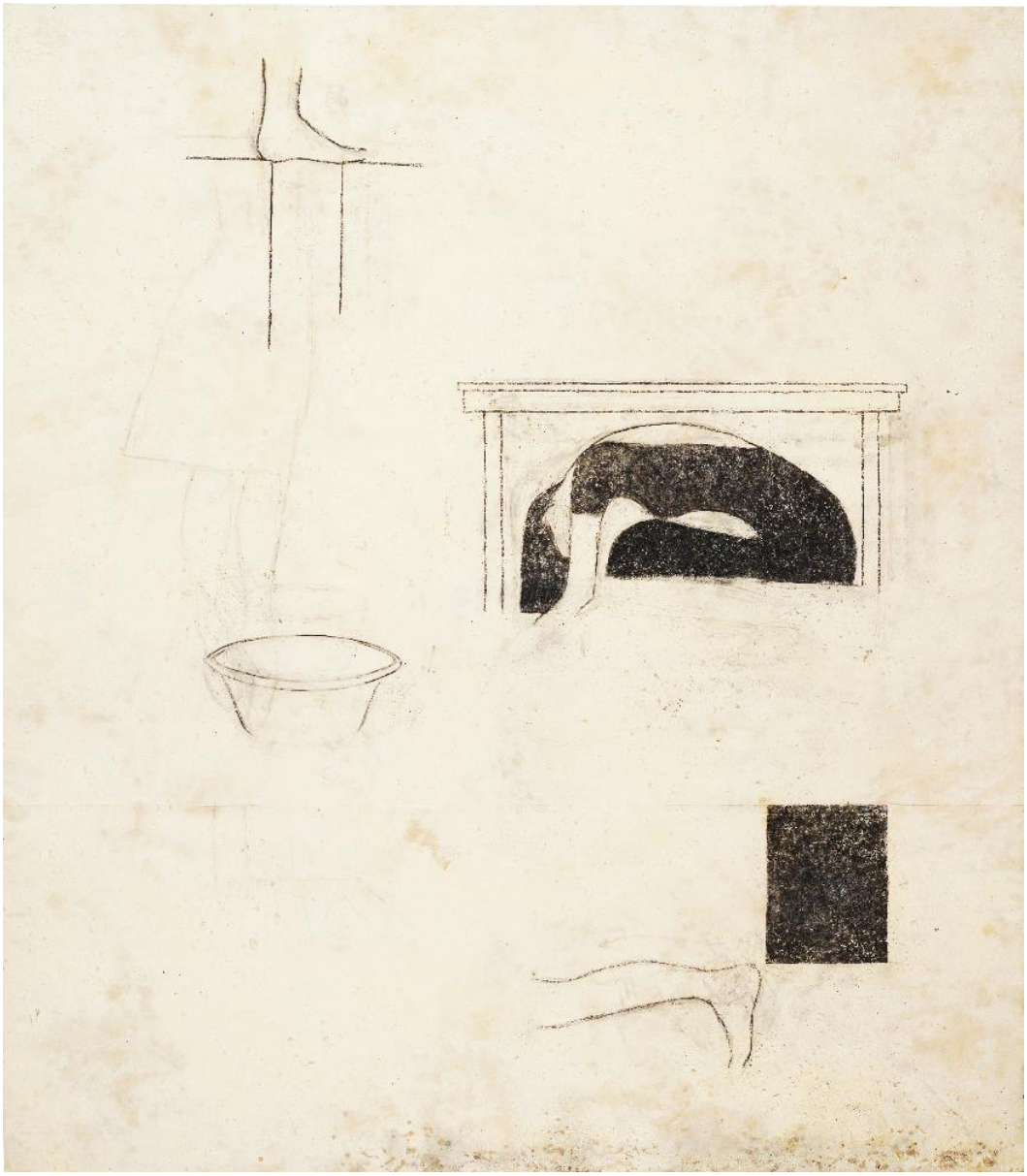


Fig. II.7: *I don´t want to go to sleep*, 1991. Poly(vinyl acetate) and graphite over canvas. Culturgest – Fundação da Caixa Geral de Depósitos.

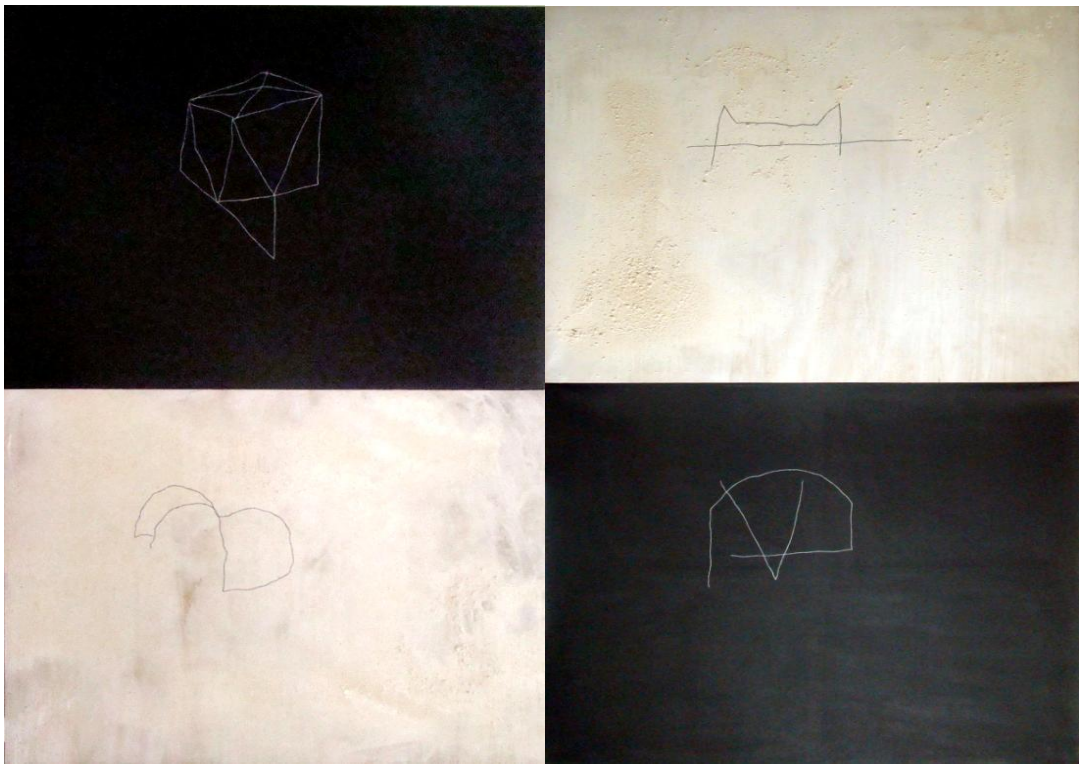
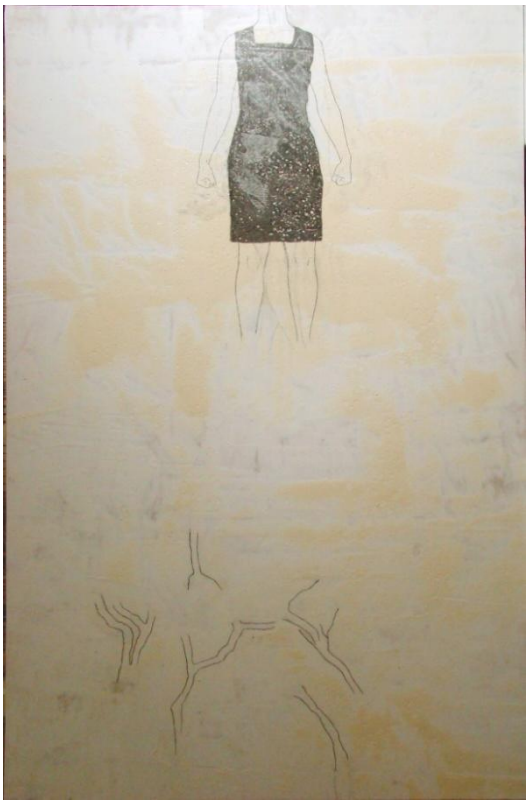


Fig. II.8: *Pintura Cega (Três instrumentos de prazer e um de dor)*, 1990. 296x380cm. Poly(vinyl acetate), chalk and graphite over canvas. Centro de Arte Moderna-Fundação Calouste Gulbenkian.

Fig. II.9: *Wasting my time with you,* 1991. 290x407,5cm. Poly(vinyl acetate), chalk and graphite over canvas. Museu Colecção Berardo.


Figs. II.10 and II.11.: Left, detail of earth in the surface of a leftover found at the artist studio. Right, Detail of *Frozen Leopard* showing the parallel marks left by the artist's hands as he draws.




Figs.II.12 and II.13.: Left, *An Involved Story*, 2008, 295x190cm.Centro de Arte Moderna-Fundação Calouste Gulbenkian. Right, detail showing yellowing of the white paint layer.

Although these are the usual materials used by Julião there are exceptions to the rule. One is the series of paintings *What makes a writer great* produced between 2000 and 2001. For those Sarmento used Robiallac and, or Sotinco household paint on paper.

The artist and museum curators claim that the white monochromatic surface of these paintings is yellowing. In an interview conducted in 2004 Sarmento already mentioned being aware of this discoloration problem. The artist also described other negative experiences as he notices that the surface is tacky and is therefore prone to damage, by imprinting or burnishing by packaging

materials. The artist's concerns are not surprising as usually these vinyl latexes have a low T_g therefore at room temperature the surface is sticky and soft.

2004-2010: *V7* + white and black dry pigments followed by acrylic gypsum

Yellowing of works from the *White Painting* series triggers changes around 2004. The discoloration started to bother the artist and he wished the paintings to retain the pristine white look they have when the paint is applied. Consequently over the usual vinyl white paint, a thin layer of diluted white gesso primer (acrylic gypsum) from *Winsor & Newton* or *Talens* is applied.

Moreover Sarmento is forced to change painting materials. With closure of the *Favrel* factory in 2008, *Cenógrafa's* production is discontinued. Julião manages to buy by weight another white pigment from Casa Varela. Analyzes of these new pigment (collected at his studio) show the white was replaced by pure rutile titanium dioxide. For the same reason *V7* is replaced with a similar glue and was called *Bizonte*. Two case-studies exemplify this period, *Inadequate Readings (Identity of Anyone)* (2004) (Fig. II.14) and *Hélder* (2008) (Fig. II.15).

a) 2010-onward: *Imofan AV44/11* + Titanium white

With the closure of *Casa Varela* in 2009 Sarmento lost his main materials supplier. However, the artist was informed that *Imofan AV44/11* emulsion was used to produce *Bizonte* glue. Therefore, nowadays Sarmento buys gallons of this emulsion, directly to the Portuguese distributor *Sarcol*, and uses the glue without further preparation with TiO_2 rutile dry pigment.

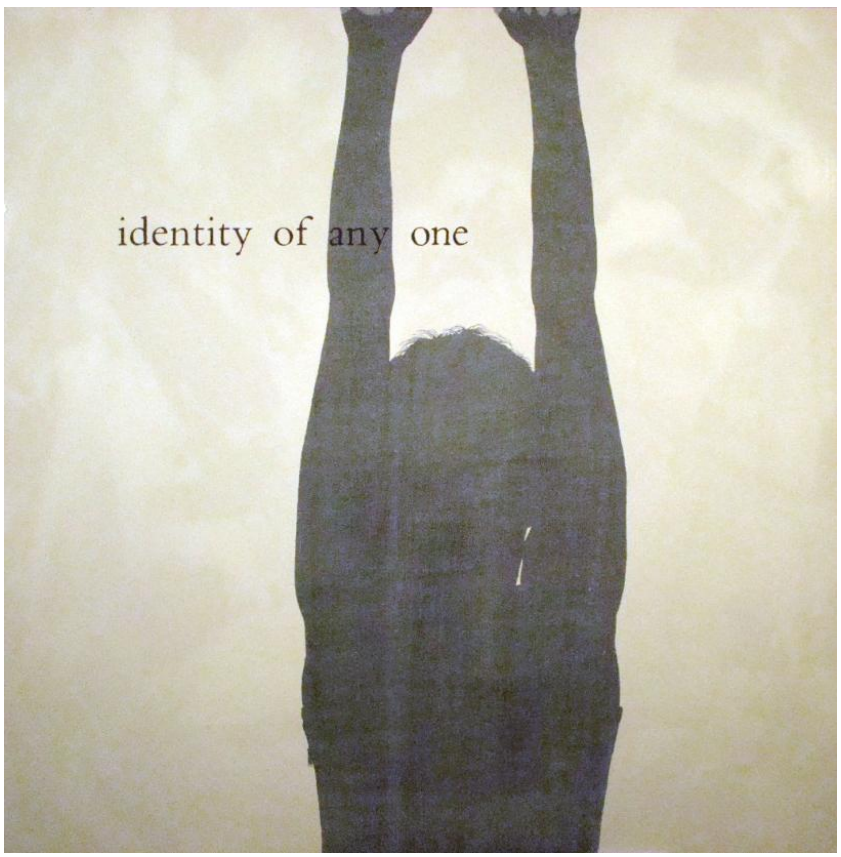


Fig II.14: *Inadequate Readings (Identity of anyone)*, 2004. 120x120cm.. Poly(vinyl acetate) on canvas. Private collection.

Fig II.15: *Hélder*, 2008. 190x190cm. Poly(vinyl acetate) and acrylic on canvas.Centro de Arte Moderna-Fundação Calouste Gulbenkian.

Besides yellowing of the white paint two of the case studies are good examples of conservation problems posed by contemporary paintings. Damage due to the low paint's T_g occurred to the work *Inadequate Readings* painted in 2004. This painting had to be treated when a piece of glass got stuck to the paint's surface during transportation. Moreover, in another painting damage caused by the inadequate choice or use of packaging materials coud also be seen. (Figs. II.16 and II.17)

Fig.II.16 and Fig.II.17: (Left) detail of *Frozen Leopard* showing damage because storage materials were stuck on the paint's surface (namely styrofoam). (Right) Detail of *Inadequate Readings*… showing damage when a piece of glass got accidentally glued to the surface.

Table II.1: Result summary of analyzes from selected case studies.

Paintings	Date	Color	Binder	Pigments and fillers
Salto	1985/86	White	PVAc + VeoVa	Anatase $CaCO_3$, $BaSO_4$
		Red	PVAc + VeoVa	Hematite, Carbon black; $CaCO_3$
		Blue	PVAc (based¤)	Ultramarine blue; carbon black
		Black	PVAc (based¤)	Magnetite $CaCO_3$
52	1985	White	PVAc	Anatase, lithopone $CaCO_3$
		Red	PVAc	Hematite, rutile Kaolin.
		White/yellowish	PVAc	Anatase, lithopone $CaCO_3$
		Yellow	PVAc	Lithopone, $CaCO_3$
		Black	PVAc	Carbon black, rutile, lithopone Kaolin
White background*	87-89	White	PVAc + DBP	Lithopone $CaCO_3$
I don't want to go to sleep	1991	White	PVAc	Lithopone $CaCO_3$
		Drawing	—	Graphite
Wasting my time with you	1991	Black	PVAc	Carbon black, $CaCO_3$
		White	PVAc	Lithopone $CaCO_3$
		Drawing	—	Graphite
Belém	1992	White	PVAc + DBP	Lithopone $CaCO_3$
		Drawing	—	Graphite
Pintura Cega...	1990	White paint	PVAc	Lithopone $CaCO_3$
		Black paint	PVAc	Carbon black
		Drawing	—	Carbon black
The Frozen Leopard	1991-1992	Red	PVAc	Burnt Umber
		White	PVAc	Lithopone $CaCO_3$
		Black drawing	—	Graphite
An Involved Story	1998	White	PVAc + DBP	Lithopone
		Black drawing	—	Graphite
Inadequate Readings	2004	White	PVAc	Lithopone $CaCO_3$
		Black	P(VAc-E-VC)	Carbon black
Hélder	2008	White top layer	Acrylic P(EA-MMA)	Rutile $CaCO_3$
		White underlayer	PVAc	Rutile $CaCO_3$
		Yellow	PVAc	Azo pigment
White background#	2010	White	PVAc + PEG	Lithopone $CaCO_3$

¤ Only two of the four samples were analyzed by Py-GC/MS which confirmed the presence of PVAc-VeoVa copolymer. In the other two due to the contamination of a synthetic glue to line the painting the interpretation of the infrared spectra is not straightforward. It can only be said that a PVAc based binder was used. It was not possible to confirm if the binder is also a copolymer.
*This is a leftover of a painting. It was kept in several studios faced down with a plastic covering it.
Mock-up done by Julião Sarmento during the workshop integrated in the Masters Conservation-Restoration course of the University.

2.5. Reflexions on Sarmento's materials and working methods

The close collaboration, unrestricted explanations and descriptions of Julião Sarmento provided invaluable information that disclosed how and why the aesthetic appearance of his paintings surfaces were obtained. It allowed to see how extensive his choice of binding media was over the years. How in the same painting different materials could be used. Even when in the 90's the materials were narrowed down to white glue and a pigment Sarmento explores the potentialities of changing the binder/pigment ratio to achieve a richness in textural effects.

Sarmento's free disposition in the use of painting materials can be illustrated by a small episode that ocured during the interview/visit to the artist´s studio in 2008. While collecting samples of paints from old paint tubes namely the Crimson red from *Rowney* PVAc paints (these paints will be discussed in the following chapter) Sarmento approached the table and with a small brush picked up a piece of this paint. He was working on a painting and used that paint on it. According to him as soon as he saw that red he new that was the colour he needed on the painting he was working. The point being, in a more recent work a piece of red from an old paint tube can now be found.

Naturally Sarmento is somehow dependent on the producers of the paint. As his main supplier (the *Favrel*) changed his raw materials and later closed, working materials and methods had to change. That is the case nowadays with the use of the pure emulsion *Imofan AV44/11*. Sarmento has noted that the emulsion in terms of consistency is not the same than when it was present in the white glue *Bizonte*. Because it is more liquid the artist and his assistant are trying to find a working method with this emulsion that will allow him to create the texture he wants.

Although most of the materials used by Sarmento are *regular* artists or, industrial paints others are not. That is the case of soil/dirt used in some paintings from the end of the 80's and in the *White Paintings* series. In the first case as an example in Just a Skin Affair from 1988 the odd colour and look of the paint layers made with the soil did give rise to some conservation concerns as to if it was a degraded paint layer or, if that was the original look of it. The question prompted its study in 2001 that established that its appearance was the original one.[19]

An important note should be made regarding Sarmento's selection of materials and their durability. In general terms Julião gives privilege to the aesthetic qualities of his materials. In his own words: "I am not going to change a millimeter of my work thinking of durability". However if alteration of the materials affects visually his works and makes it contradictory to his purposes Sarmento will make changes. That was the case of the *White Paintings* serie.

The informations gathered raised awareness for the need to collect as much data from the artist as possible. Moreover to collect and analyze as much of the paints he used and still uses as possible because, a paint's formulation is complex and producers are know to change it. For instance the *Sabu* paints used in the 80's and found in one of the case studies show they are based in the copolymer of PVAc-VeoVa. Meanwhile, the *Sabu* used in the painting *Inadequate readings* shows the terpolymer formulation P(VAc-E-VC). Therefore on one hand a comprehensive selection of paints and analyzes had to be done. On the other hand the results narrowed the choice of materials to be subjected to aging and how to prepare accurate reproductions. Besides, acess to some of his painting materials provided this reaserch with historical paint products and naturally aged samples.

III. Results on the molecular characterization of vinyl binders and colored paints used by Sarmento

Molecular characterization of binding media, pigments and additives present in the paint's formulations is fundamental to understand their influence on the film's lifetime. It is generally accepted that complete characterization of the additive system in a latex paint is impossible because, the low concentrations in which they are used make analytical identification very difficult.[8] Moreover a comprehensive identification of the major components can only be achieved using a multi-analytical strategy therefore, characterization of the paints was carried out by micro Fourier transform infrared spectroscopy (μ-FTIR), by Py-GC/MS whenever possible, by micro Raman and by micro X-Ray Fluorescence (μ-XRF).(see Appendix II Analytical techniques and methods)

The paints selected to be studied are mainly products that were produced by *Favrel*, sold at *Casa Varela* and used by Julião Sarmento. Most of the products were obtained at *Casa Varela*, at Sarmento's studio or, directly from the Portuguese distributors. Description of the samples and full results are assembled in Appendix III. Molecular characterization of vinyl binders and colored paints used by Sarmento. Some old paint tubes of *Rowney PVAc* paints, one of the first vinyl waterborne paints to be produced in the UK by George *Rowney* & Company, were found in the artist's studio. According to the manufacturer these PVAc paints were formulated with polyvinyl acetate and $BaSO_4$ and colour was provided with standard synthetic organic pigments, titanium dioxide, synthetic iron oxide, and natural iron oxide pigments. This brand was discontinued in 1988.[19] Research included them for characterization purposes and their content was analyzed. Table III.1 contains the summary of the composition of all the vinyl based products analyzed. (Appendix III contains all the analytical results)

3.1 *Vulcano V7* and *Bizonte*

The aqueous dispersion of poly(vinyl acetate) used in *Vulcano V7* was changed at least four times since it was introduced in the market in 1957.[5, 6, 19, 38] After the factory's closure *V7* was renamed *Bizonte* and it could still be purchased at *Casa Varela*. The container was similar to the *V7* white glue except for the label. Information regarding *V7* and *Bizonte* and identification of the raw emulsions used in their production is systematized in Table III.1.

Fig. III.1: White glues used by Sarmento to create his paintings and one of his techniques of application.

[19] Information provided by Taylor Gibbons of the Marketing Department of the *Daler-Rowney Limited* company in the UK.

Table III.1: Summary of the analyzes results done on vinyl paints used by Julião Sarmento.

Products	Dates	Polymer	Plasticizers	Pigments	Fillers
		White glues			
Vulcano V7	2004	PVAc	DiBP	—	—
Bizonte	2009	PVAc	DPGDB DEGDB	—	—
Vinamul 3469	2009	PVAc+PVC + PE	—	—	—
***Imofan* AV 44/11**	2009	PVAc-VeoVa	DiBP	—	—
		Old Sabu paints			
Binder	(Unfortunatley the artist could not recall when they were bought)	PVAc	DBP	—	—
White		PVAc-VeoVa	DBP	Anatase + Rutile + lithopone	Kaolin
Black		PVAc-VeoVa	DBP	Iron oxide + carbon black	Kaolin + $CaCO_3$
Blue		PVAc-VeoVa	—	Ultramarine	Kaolin
		Modern Sabu paints			
White	2007	PVAc-PVC-PE	—	Rutile + traces of anatase; lithopone	$CaCO_3$
Black	2007	PVAc-PVC-PE	—	Iron oxide + traces of TiO_2	$CaCO_3$
		Rowney paints			
Binder	(Unfortunatley the artist could not recall when they were bought)	PVAc (hydrolyzed)	DBP	—	—
Violet		PVAc	DBP	Azo pigment	$CaCO_3$ + Kaolin
Black		PVAc	DBP	Carbon black	—
Blue		PVAc-PE +acrylic?	DBP	Ultramarine	—
Yellow		PVAc-PE	DBP	Azo pigment	$BaSO_4$
Crimson		PVAc-PE+ acrylic?	DBP	Azo pigment	$BaSO_4$
White		PVAc-PE+ acrylic?	DBP	Rutile	$BaSO_4$

Infrared spectra of both glues contain all the spectral signatures of poly(vinyl acetate). The ester group produces an intense band at 1740cm^{-1} due to carbonyl stretching while the absorption at 1240cm^{-1} is due to stretching C-O-C of the ester linkage.[96] Methyl bending absorbs at 1370cm^{-1} and is more intense than the methylene bending absorbing at 1470cm^{-1} because the CH_3 group is directly attached to the carbonyl group.[96] The pyrograms of both binders contained the characteristic fronting peak and mass spectra corresponding to acetic acid (m/z=43, 45 and 60) (due to side group elimination during pyrolysis) and to benzene (m/z=78) (the polyene backbone that results after side group elimination).[2] (See Appendix III) Diisobutyl phthalate was

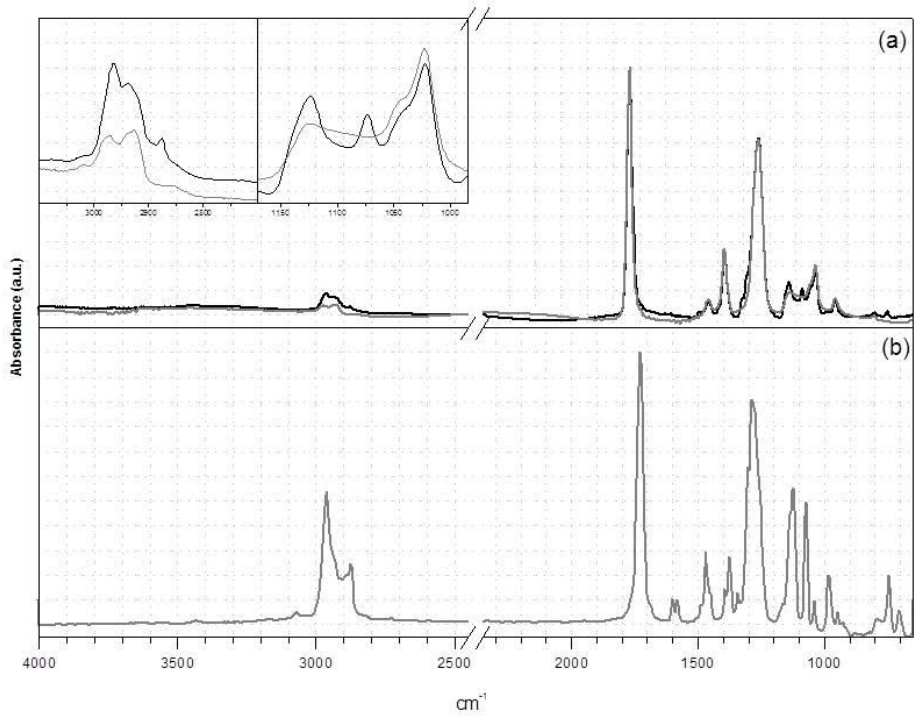
identified by Py-GC/MS by the characteristic mass spectra with m/z=149 which is characteristic of all dialkyl phthalate plasticizers.[2] The mass spectra and the retention time of its very intense peak allowed distinguishing it from other phthalates. Identification and quantification of its content in the Vulcano glue suggests that ≈21% of plasticizer is added to the emulsion. The phthalate is also detectable by μ-FTIR.

Table III.2: Producers and distributors of the raw emulsions used in white glues sold by *Favrel*

		Vulcano V7		
Date	**Raw material**	**Producer and/or distributor**	**Formulation**	**References**
1957-1987	*Synresil LM15*	Produced and distributed by Portuguese company *Synres*	Vinyl emulsion*	[5, 38]
1987-1999/2000	*Imofan AV44/11*	Produced by *Celanese*, GMBH Distributed by *Sarcol*	Vinyl emulsion[#]	[5; 19, 38]
2000-2006[#]	*Albucol 25P4*	Produced by *Proadec*, UK[20] Distributed by *Globalcor*	PVAc + DiBP	(according to the analyzes)
		Bizonte*		
2006-...	*Albucol 25P4#*	Produced by *Proadec*, UK Distributed by *Globalcor*	PVAc + DiBP	(according to the analyzes)
...-2011	*Imofan AV44/11*	Produced by *Celanese*, GMBH Distributed by *Sarcol*[21]	PVAc-VeoVa + DiBP	

* No other information on the chemical nature of the polymer used was found.
[#] The same happens for this raw material and although the same designation is used for the *Celanese* emulsion produced and analyzed in 2011 there is no evidence that the formulation is the same.

[20] According to *Globalcor* this resin was discontinued in 2006. According to the same source *Proadec* is an English company that no longer produces resins.
[21] According to information provided by *Sarcol Química*, the Portuguese distributor. The producer *Celanese* could not provide any more information because this is not the designation given by company. The technical sheet provided by *Sarcol*, only contains information on the Portuguese name *Imofan AV 44/11*



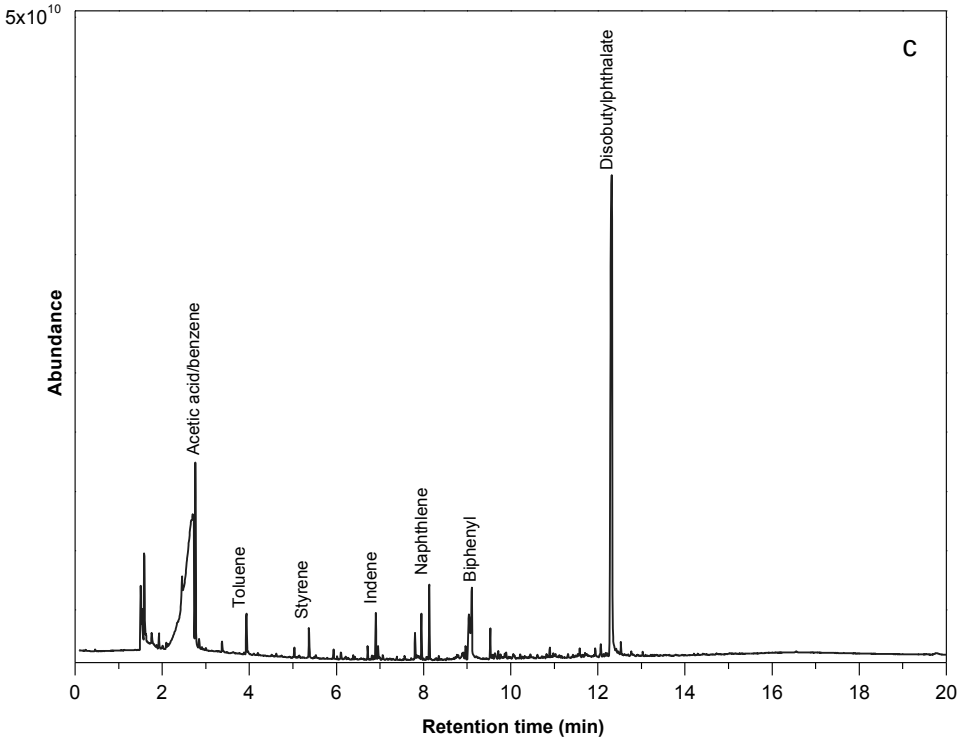


Fig.III.2 – (a) FTIR spectra of *Vulcano V7* emulsion (—) and PVAc (—) and (b) of DiBP.
(c) pyrogram of *Vulcano V7* a PVAc homopolymer.

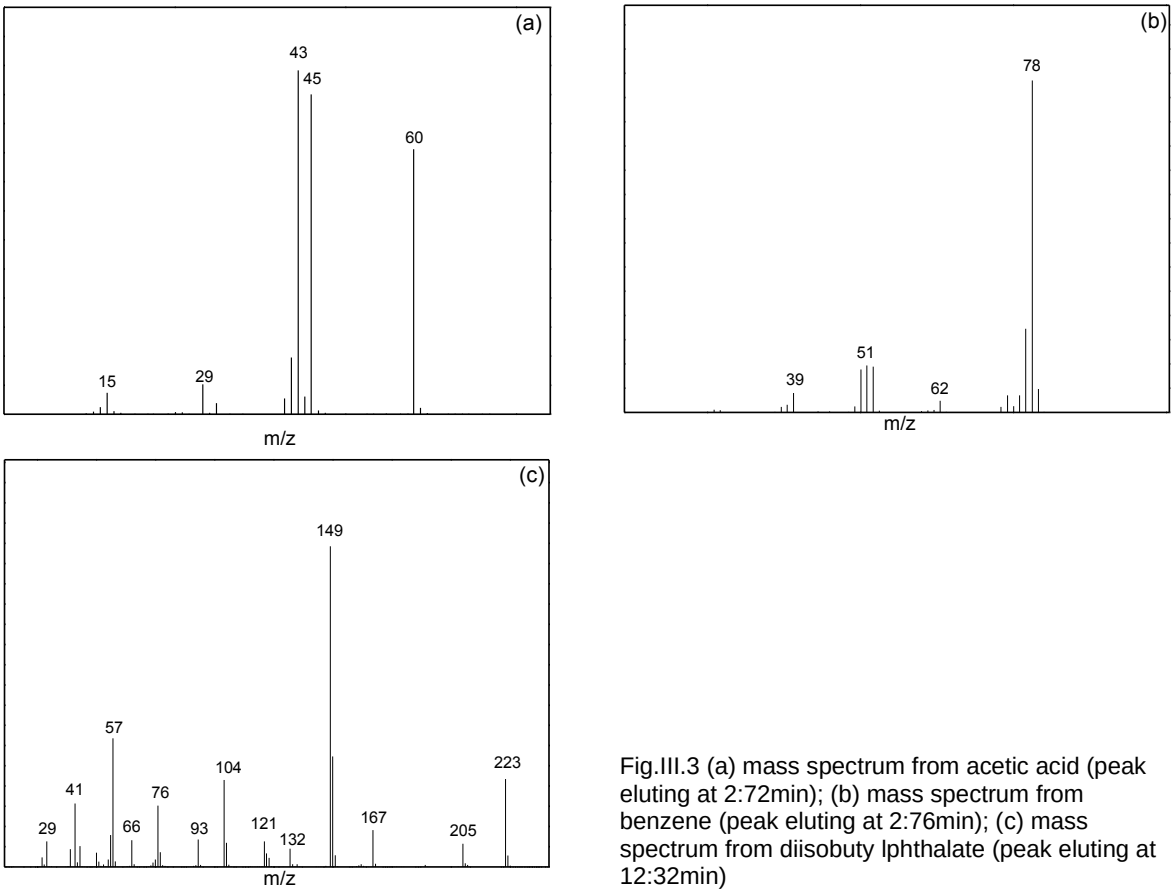


Fig.III.3 (a) mass spectrum from acetic acid (peak eluting at 2:72min); (b) mass spectrum from benzene (peak eluting at 2:76min); (c) mass spectrum from diisobuty lphthalate (peak eluting at 12:32min)

Imofan AV44/11 is described in the technical sheet provided by the Portuguese distributor *Sarcol* as a vinyl homopolymer. And although the infrared spectra is very similar to the spectra of a PVAc homopolymer (Fig.III.4 a), by Py-GC/MS a copolymer of poly(vinyl acetate) and vinyl versatate with diisobutyl phthalate used as an external plasticizer was identified. (Fig. III.4 b and III.5 and 6) The VeoVa component was identified by its characteristic fronting profile, the mass spectra and molecular weight typical of fatty acids.[2]

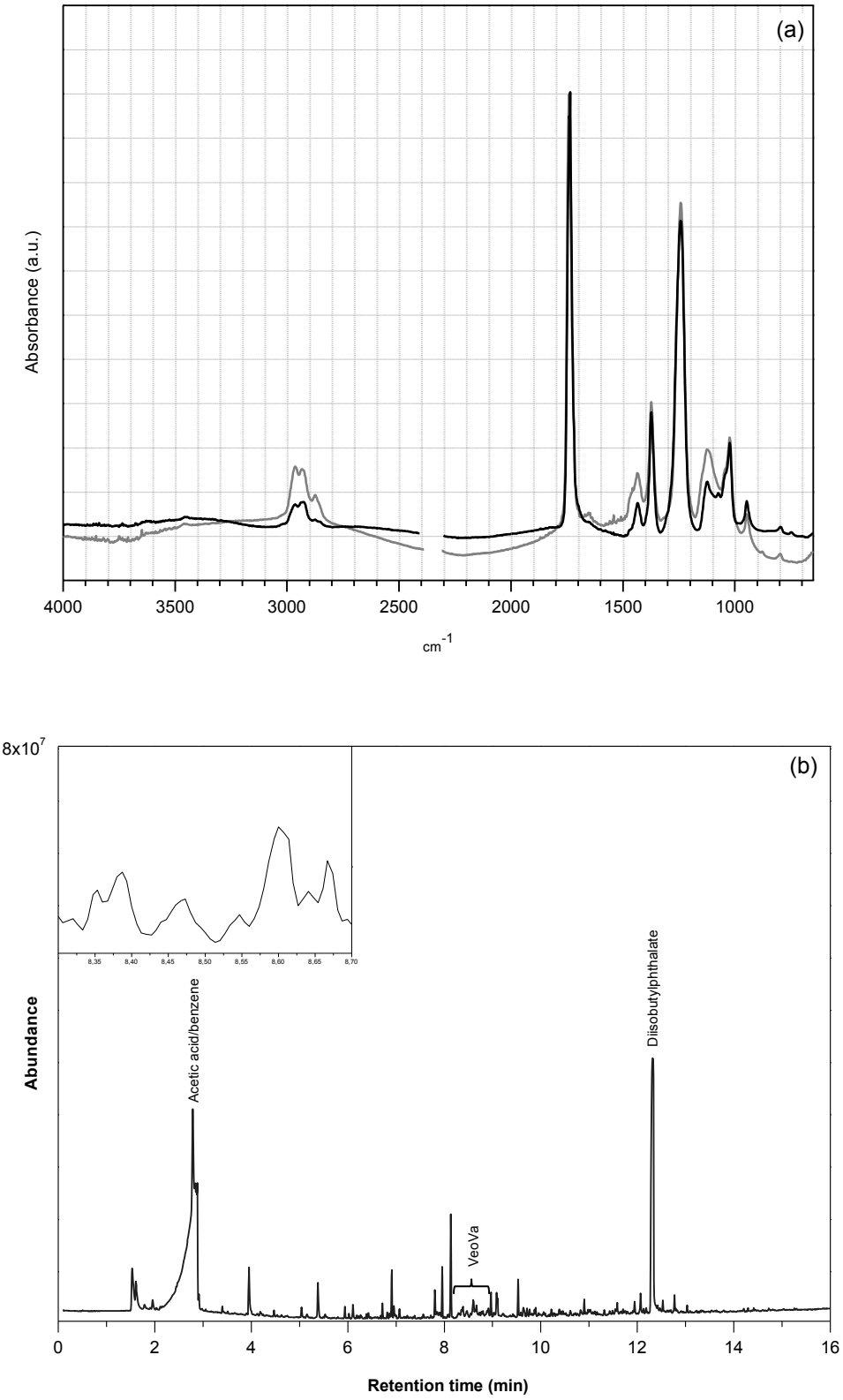
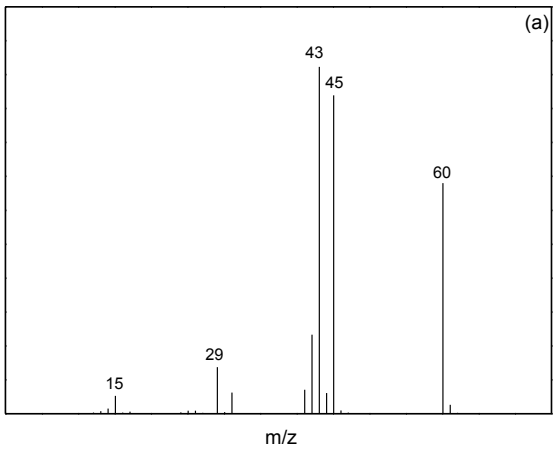
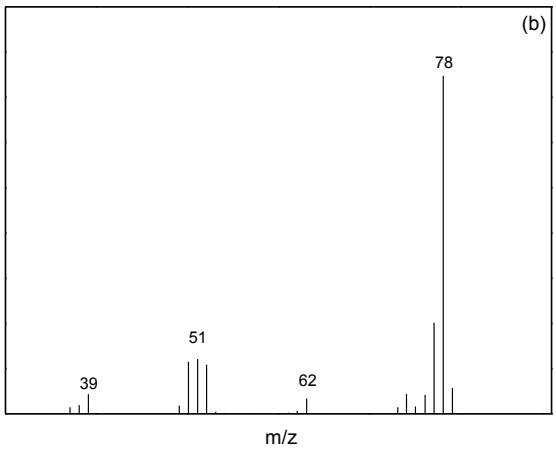


Fig. III.4. (a) Infrared spectrum of *Imofan AV 44/11* (—) and of *DM23* (—) a PVAc-VeoVa copolymer produced by *Resíquimica* and (b) pyrogram of *Imofan AV 44/11*. Inlay shows the peaks that indicate the VeoVa fraction.





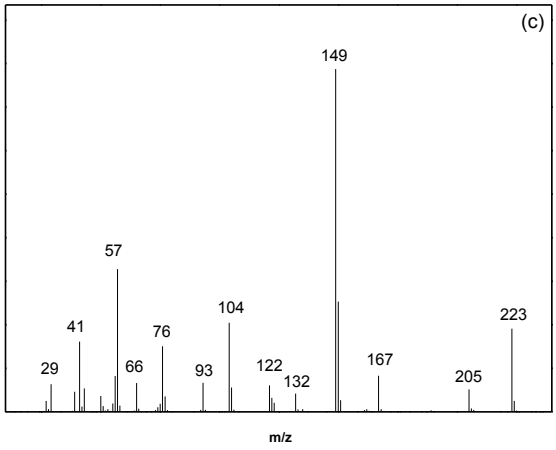
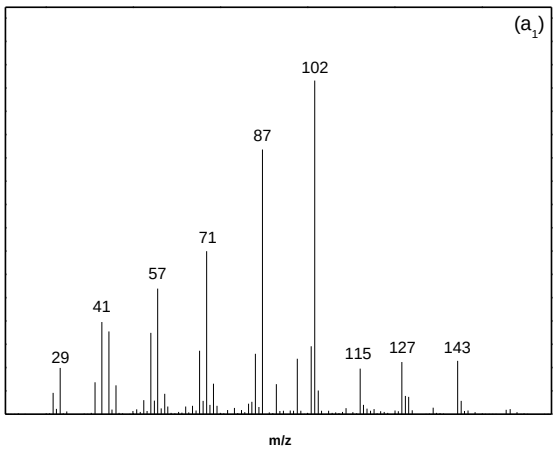
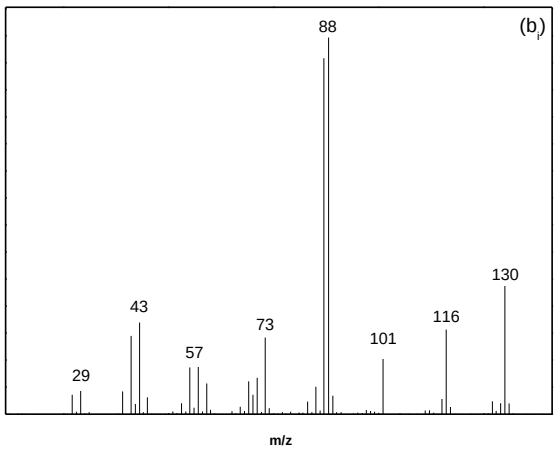


Fig. III.5. (a) mass spectrum from acetic acid (peak eluting at 2:79min); (b) mass spectrum from benzene (peak eluting at 2:89min); (c) mass spectrum from diisobutyl phthalate (peak eluting at 12:32min).





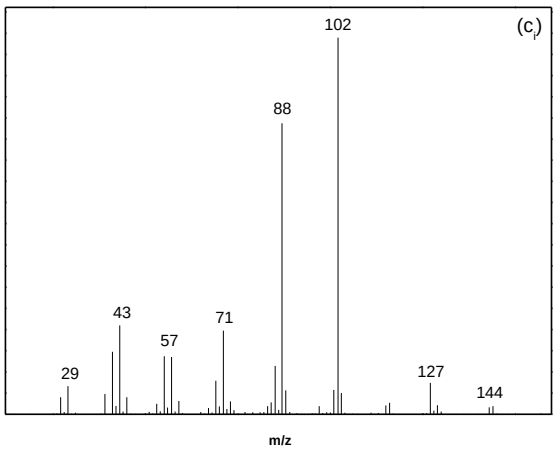


Fig. III.6. (a_1, b_1, c_1) mass spectra from VeoVa component shown in the pyrogram inlay in Fig.III.4.

Table III.3: Wavenumber and band assignment for the studied homopolymer emulsion and copolymers.

Band assignment	PVAc (solution Aldrich)	*V7* PVAc emulsion	*Sabu* emulsion binder	PVAc-VeoVa emulsion (DM23)	DBP	DiBP
vC=O overtone	3452	3450	3450	3457	3437	3433
vC-H	—	—	—	—	3070	3072
v_{as}C-H (CH_3)	2971	2963	2962	2964	2962	2963
v_{as}C-H (CH_2)	2926	2939	2936	2933	—	—
v_sC-H (CH_3)	—	2877	2874	2875	2874	2876
vC=O	1740	1740	1740	1740	1729	1730
vC-C in aromatic compounds	—	1599	1599	—	1605	1599
	—	1580	1580	—	1586	1581
	—	1470	1464	—	1488	—
δ_{as}C-H (CH_3), δC-H (CH_2)	1434	1433	1433	1434	1462	1469
δ_sC-H (CH_3)	1374	1373	1373	1373	1385	1375
vC-O of **(CO)O**	—	1288	1289	—	1285	1286
	1243	1243	1243	1241	—	—
vC-C	1124	1123	1123	1124	1126	1123
δC-H ring bending*	—	1073	1075	—	1073	1073
vC-C	1047	1047	1047	—	1041	1039
vC-O of **(O-CH)**	1023	1022	1022	1023	—	—
vC-C	—	981	—	—	—	**981**
ρ_rC-H (CH_2)	947	950	946	946	943	946
Out of plane C-H ring, bending and ring puckering	796	796	795	796	—	**795**
	—	745	748	—	744	745

3.2.Old *Sabu* binding medium

Regarding the *Sabu* paints (see Table III.4) there is previous data collected at *Casa Varela* [5, 19] Also The study of a hand painted catalogue from the 60's revealed that the 21 colours present contain a PVAc binder.[5] Some old *Sabu* paint jars were found in Sarmento's studio and were analyzed for characterization purposes. The three pigmented white, blue and black paints were produced with a PVAc-VeoVa copolymer. But, the jar containing pure *Sabu* binding medium is an homopolymer emulsion plasticized with DBP. It is worth to mention that the old *Sabu* paint jars were labeled as Tempera Acrílica (Acrylic Tempera) while the results reveal that all are vinyl based. (Fig.III.8 and Table III.4)

Table III.4: Producers and distributors of the raw emulsions used in the production of *Sabu*

***Sabu* from Casa Varela**					
Sample	**Date**	**Producer and/or distributer**	**Raw material**	**Formulation**	**Source of information**
—	1963-….	**—**	**—**	Phenol-urea	[38]
—	…-1978-…	**—**	*Vinamul*		
—	1985	Possibly produced by Vinyl Products; distributed by E.Brunner	*Vinamul 6975*	PVAc-VeoVa	
Binder	—	**—**	**—**	PVAc + DBP	Paint tubes offered by Sarmento
Colored	—	**—**	**—**	PVAc-VeoVa + DBP	
Colored *	2001-2006[#]	Produced by Celanese, GMBH; distributed by Globalcor, S.A.	*Vinamul 3469*	P(VAc – E – VC)*****	Emulsion offered by Globalcor, S.A.

* The paints were analysed by µ-FTIR and Py-GC/MS. According to the producer this resin is a terpolymer and not a blend of the three polymers.

[#]The production of these paints was discontinued

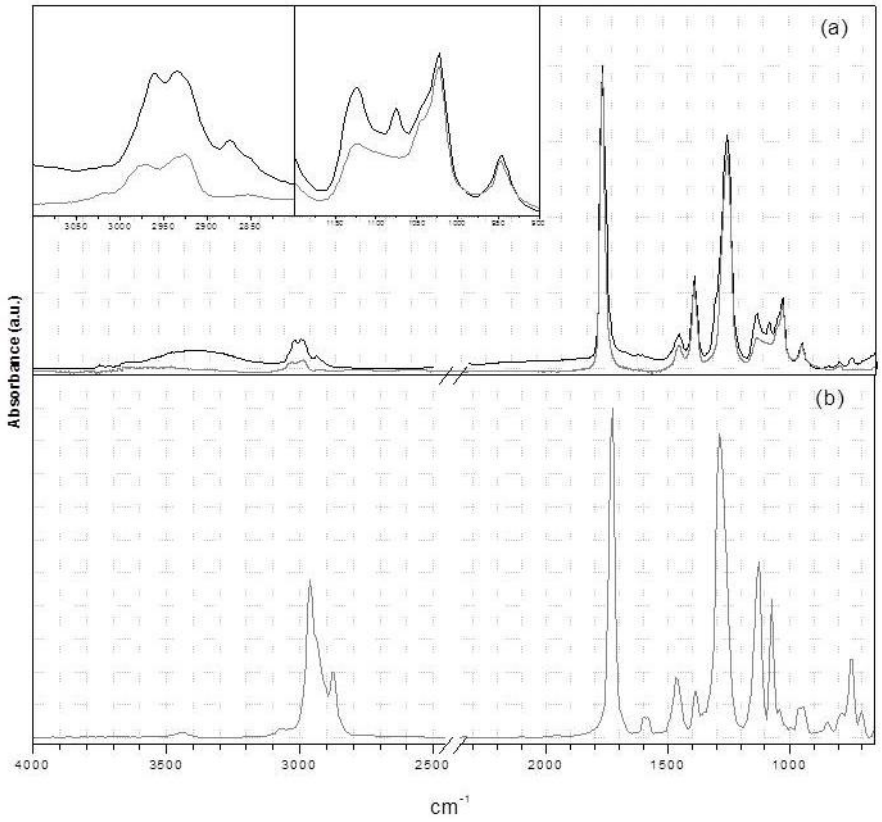


Fig.III.7 – (a) FTIR spectra of the emulsion *Sabu* binding medium (—) and PVAc (—) and (b) of DBP.

3.3.Old colored *Sabu*: PVAc-VeoVa copolymers

Unlike the pure *Sabu* binding medium the analyzed old *Sabu* colored paints contained a PVAc-VeoVa copolymer. This might indicate that the jars are from different periods and the raw emulsion used by *Favrel* in their production was changed. The VeoVa component of the copolymer was clearly identified by Py-GC/MS as several characteristic fronting peaks with m/z=87 and 88 eluting between 8 and 9 minutes. [e.g. 2, 97] An extra plasticization effect was obtained by adding DBP. This phthalate was identified by its m/z=149 and its retention time. (Fig. III.9 and III.10)

Fig. III.8: Images of old paint jars of *Sabu* produced by *Favrel*. The yellow jars are of pigmented colour paints. The smaller white one is from the pure binding medium. All labels contained the designation *Tempera Acrílica.*

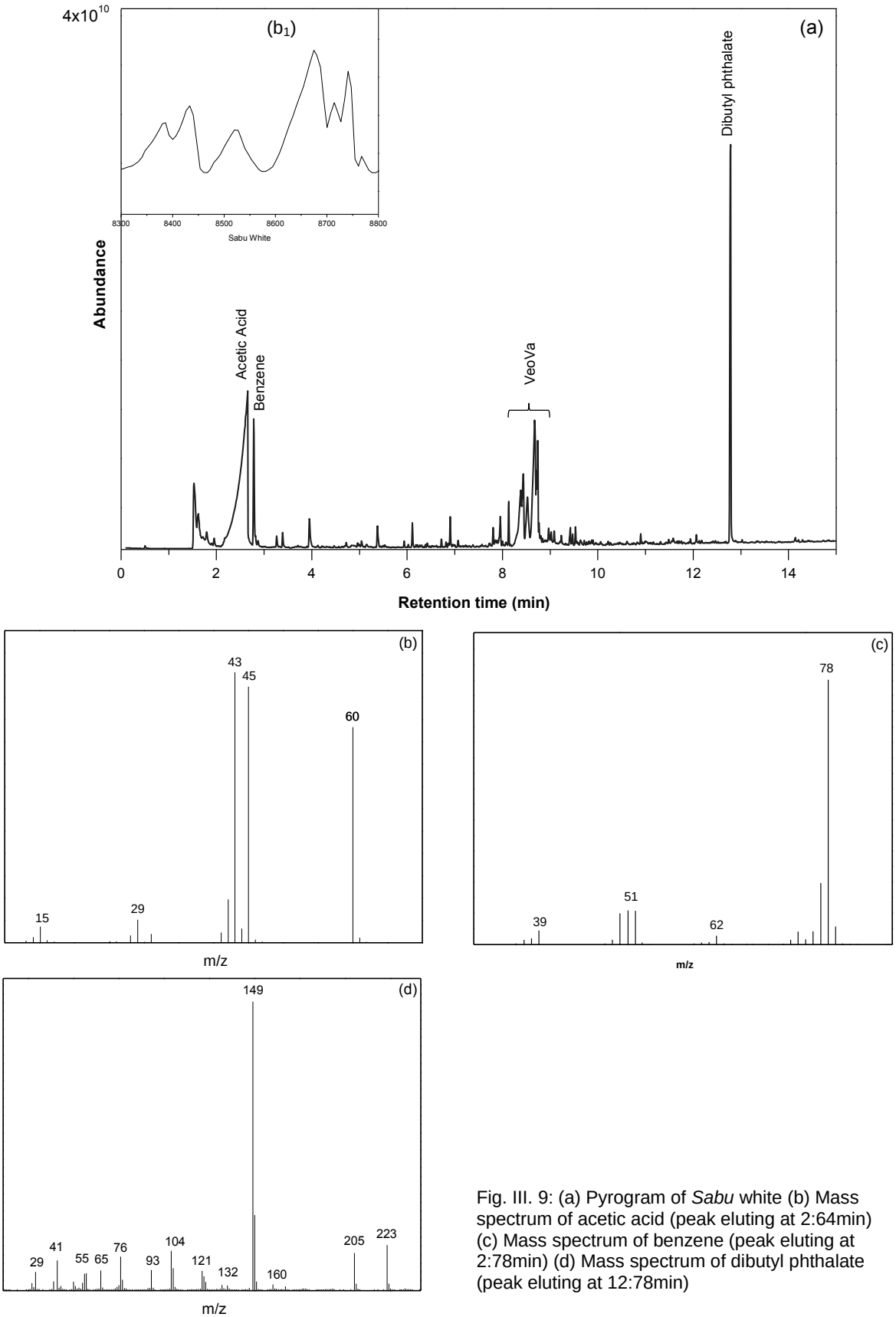


Fig. III. 9: (a) Pyrogram of *Sabu* white (b) Mass spectrum of acetic acid (peak eluting at 2:64min) (c) Mass spectrum of benzene (peak eluting at 2:78min) (d) Mass spectrum of dibutyl phthalate (peak eluting at 12:78min)

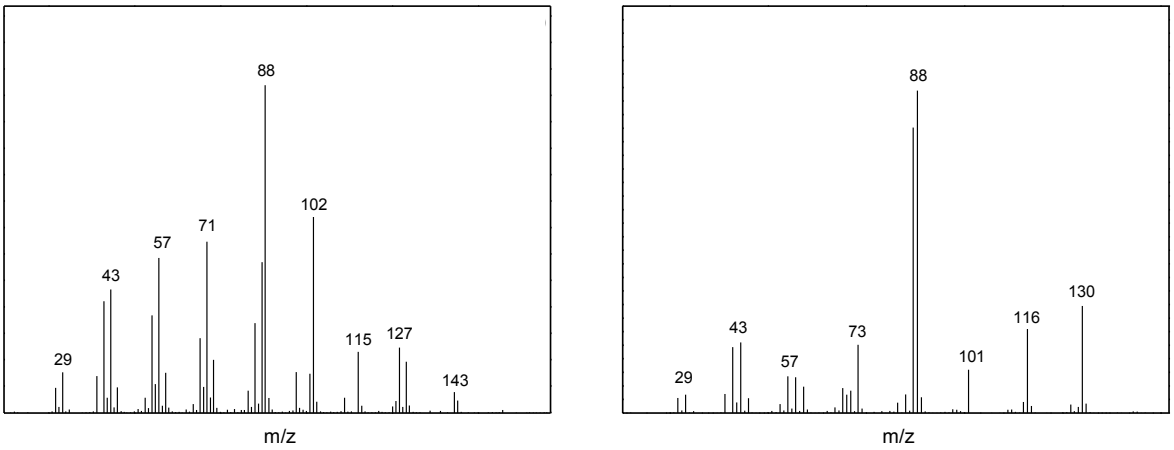


Fig. III. 10: (a_1) and (b_1) Mass spectrum of neodecanoic acid (peaks eluting at 8:38 and 8:63min) from the pyrogram show in Fig. III.9.

3.4. Modern colored *Sabu*: PVAc-PE-PVC terpolymer

To our knowledge from 2001 until the factory closed the binding medium used in the *Sabu* artist's paints was *Vinamul 3469*. According to the producer *Celanese* the emulsion contains a P(VAc-VC-E) terpolymer and not a blend of the three polymers. This company no longer produces this product because they were not satisfied with their properties and aimed at offering coatings with better performance.[22]

The pyrogram of this emulsion shows the PVC content with the mass spectrum of hydrochloric acid. (Fig. III.11) The infrared spectrum is however not that straightforward in showing the PVC content. (Fig. III.12) In infrared the most significant differences between the PVAc homopolymer and the *Vinamul 3469* occur in C-H stretching region between, 3100-2500cm^{-1}. Two medium intensity bands occur at c.2935cm^{-1} and c.2861cm^{-1}. Wavenumbers do not match typical values of any of the monomers therefore it may be argued that the absorption results from the combination of individual C-H stretching bands from the three monomers. Furthermore the *Vinamul*'s reference spectra is very similar to the reference spectra of poly(vinyl acetate) in the fingerprint region. However, in that range contribution of polyethylene may account for the following bands: at c.1458cm^{-1} the CH bending vibration of PE (neither PVAc nor PVC shows any infrared absorption at this wavenumber); and, at 670cm^{-1} although this band could also be due to C-Cl stretching. With the exception of the small bands at 800 and 670cm^{-1}, which can be tentatively assigned to the poly(vinyl chloride) monomer, all the other PVC absorption bands appear to be masked by the absorption bands of the PVAc.

[22] Information provided by *Celanese Emulsions* GmbH. During research a close collaboration between the producer was established. Through email it was possible to gather information on the production of this emulsion and acquire technical sheets.

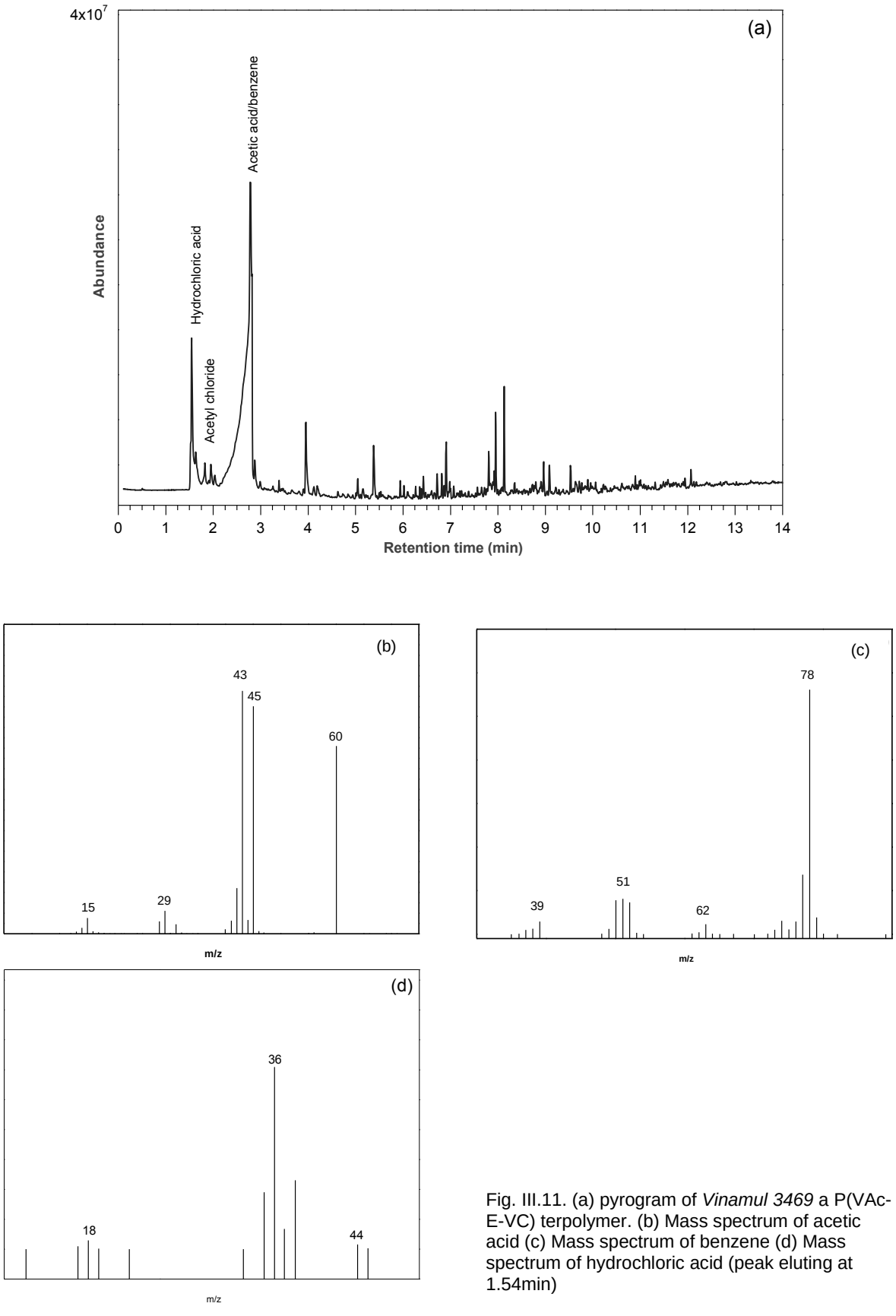


Fig. III.11. (a) pyrogram of *Vinamul 3469* a P(VAc-E-VC) terpolymer. (b) Mass spectrum of acetic acid (c) Mass spectrum of benzene (d) Mass spectrum of hydrochloric acid (peak eluting at 1.54min)

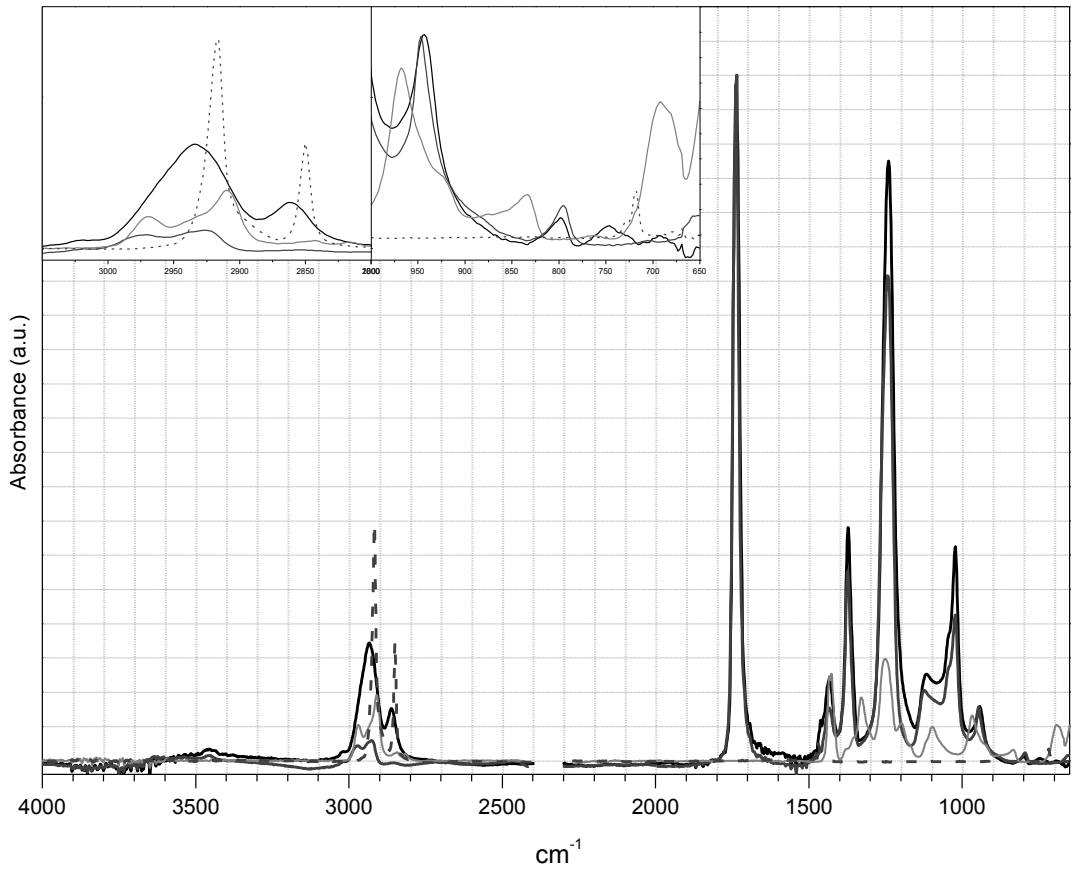


Fig.III.12 – Infrared spectra spectra of the emulsion *Vinamul 3469* (—), PVAc (—), PVC (—) and PE (- - -).

Table III.5: Wavenumber and band assignment for the studied terpolymer.

Band assignment	PVAc (solution Aldrich)	PVC	PE	P(VAc-E-VC) (*Vinamul* emulsion)
vC=O overtone	3452	—	—	3446
ν_{as}C-H (CH_3)	2971	2969	—	—
ν_{as}C-H (CH_2)	2926	2909	2916	2934
ν_{s}C-H (CH_3)	—	2843	2850	2860
vC-H	—	2814	—	—
vC=O	1740	—	—	1734
δ_{as}C-H (CH_3), *δC-H (CH_2)*	1434	1433	1472	1460
	—	1426	—	1434
δ_{s}C-H (CH_3)	1374	1381	—	1372
vC-O of (CO)O	—	1357	—	—
δC-H (CH-Cl)	—	1329	—	—
	1243	1251	—	1236
vC-C	1124	1199	—	1116
vC-C	1047	1098	—	1044
vC-O of (O-CH)	1023	—	—	1022
	—	967	—	—
vC-C	947	836	—	943
	—	—	—	—
vC-Cl[#], ρ_{r}C-H (CH_2)	796	764	—	798

[#] Strong bands in the 800-600cm^{-1} region are characteristic of the C-Cl stretching. [98] This vibrational mode is very sensitive to its environment (rotational isomeric states) resulting in a multiplicity of bands that can be attributed to the C-Cl. Resolving and assigning this vibrations (750-550cm^{-1}) has been the subject of several extensive investigations. [99]

3.5.*Rowney* PVAc paints

With some exceptions and until it was closed around 2011 Sarmento acquired most of his painting materials in *Casa Varela*. Not only because everything was cheaper but, also because António Varela was his colleague during the year Sarmento was enrolled in Arquitecture in the Escola de Belas Artes de Lisboa and would make him special prices.

Rowney PVAc paints were one of these exceptions (Fig. III.13). In three of the six colored paints analyzed a vinyl-acrylic copolymer was detected. The other three coloured paints and the unpigmented binder contained a PVAc homopolymer. Dibutyl phthalate was found in all the analyzed paints.

Fig. III.13: *Rowney* PVAc paints manufactured by *George Rowney & Company Lda*. used by Sarmento and kept in his studio.

3.6. The pigments and Fillers

Pigments are finely ground crystalline solids that dispersed in the paint are responsible for the coating's color and covering power. Pigment identification is crucial to understand a paint's aging behavior as pigments can have a significant influence in the photochemical stability of the binder. By absorbing and/or screening the light they can exhibit a protective effect; or, they may be photoactive and sensitize the photochemical degradation of the polymer.[100] Because the relevant pigments used by Sarmento since the 90´s are the white and black pigments and these could be related to conservation problems observed in his works an overview of these pigments is presented below.

3.6.1.*Cenógrafa* white: Lithopone

Lithopone is an intimate mixture of barium sulphate and zinc sulphide precipitated from a solution of barium sulphide and zinc sulphate.[101] Commercial typical grades of lithopone contain 28-30% of ZnS and 72-60% of $BaSO_4$.[102] In 1920 it was produced by coprecipitation and subsequent calcination of a mixture of zinc sulphide and barium sulphate and was a relatively new pigment in

the household paint industry.[102] Lithopone's high hiding power (ZnS *n*=2.37 [1]), cheaper production and ease of working turned it into an important white pigment.[101] Although its production declined since the early 50s it is still valued due to its good light scattering ability. [102] Because this white pigment is photochromic[23] early literature reports, as early as 1870, stated that lithopone appeared black at day and white at night.[103] Blackening due to the action of light was attributed to the formation of metallic zinc.[103] Literature from 30's also mentioned that this reversible process occurred due to exposure to UV light, especially in the presence of moisture.[104] Darkening was overcome by coating the pigment particles with zinc oxide, aluminum oxides or magnesium hydroxide.[101] Currently treatment and stabilization of the zinc sulfide is done by incorporation of cobalt in the ZnS lattice.[102] Other references also mention that sulphide pigments are known to oxidize and form sulphates.[102] Barium sulphate's refractive index is high (*n*=1,64 [102]) therefore it favorably affects opacity. It is chemically inert, with good light fastness and weather resistance.

While the presence of barium sulphate was easily confirmed by µFTIR, evidence that zinc sulphide was present could only be achieved with µRaman because ZnS absorption falls at the far IR region (c.310cm^{-1}).[105] Reference µRaman spectra of $BaSO_4$, ZnS and zinc white (ZnO) were acquired and zinc sulphide showed a characteristic absorption at c.340-350cm^{-1}.(Fig. A3.5, Appendix III) That characteristic absorption was used to identify it in the raw materials used by Sarmento and its presence in case-studies. It could also be distinguished from ZnO which has a characteristic band at 438cm^{-1}.[105-107] Although, in some cases the results were straightforward in others it was found difficult to separate ZnS absorption from background fluorescence. This occurred especially when the pigment was not analyzed as a dry powder but when it was mixed with the binder. XRF can not be used to ascertain it's presence as it only identifies the presence of the chemical elements. Only Zn, Ba, and S would be detected without discerning if it is from zinc oxide, barium sulphate or, from lithopone.

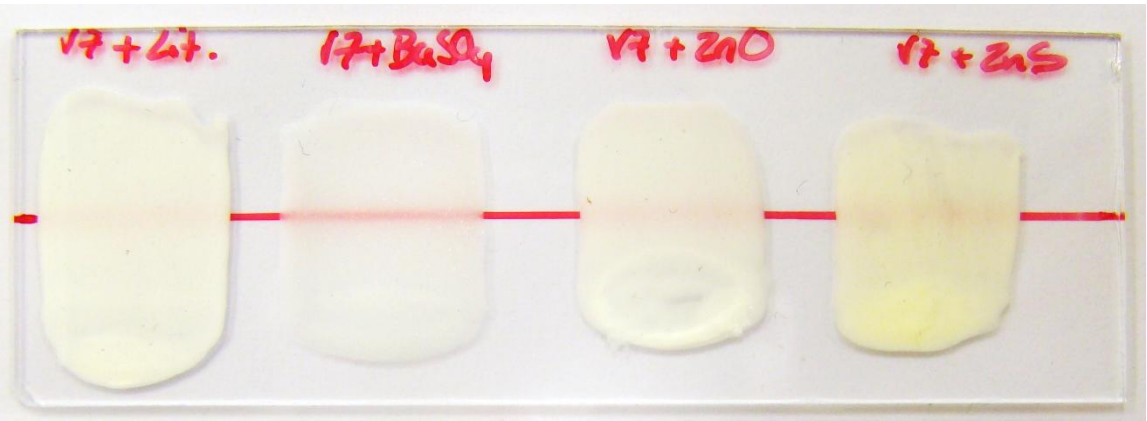


Fig. III.14 – Figure showing the diference of opacity between the white pigment lithopone and zinc oxide white and barium sulphate. Zinc sulphide without the presence of $BaSO_4$ shows a yellowish tone. (all paints were created with *V7* in a proportion of 70-30% binder/pigment ratio and were apllied with a film applicator to achieve the same thickness)

[23] Photochromic materials change their colour when are exposed to a certain radiation and reverse when that radiation is removed.[103]

3.6.2.Titanium dioxide

TiO_2 is currently the most important white pigment for artists and exists in three morphological crystalline forms. While the two forms anatase and rutile were widely used at commercial scale [1] the brookite form was never used commercially as a pigment. [37] Anatase was the first to be used however it was substituted by the rutile form which has higher hiding power (rutile *n*=2,73 [102, 61]; anatase *n*=2,55 [1; 102]), higher stability and higher hiding power/cost ratio.[26] Nowadays the use of anatase as an artist's pigment has practically disappeared.[108]

The rutile form of titanium dioxide is known to be photoactive however, surface treatments effectively stabilize the pigment[24] [61] and pigment's photoreactivity is directly related to the coating.[110] Titanium dioxide can be coated with inorganic or organic media, for the former alumina, silica, transition metal phosphates and acetates (manganese, cobalt, zinc, antimony) have been used.[61] Silica (SiO_2) and alumina (Al_2O_3) coatings provide pigments with low photoreactivity while alumina coatings provide medium reactivity pigments.[110] Other references describe a double layer: silica is used for the inner layer followed by and outer layer of hydrated alumina ($Al(OH)_x$).[30] For general purpose paints usually 2-5% (w/w) coatings are used while for greater resistance to weathering a heavier coating of 7-10% (w/w) is preferred.[37] Pigment dispersion and particle size also influence pigment stability. The smaller the particle size, the bigger the surface area, the bigger the reactivity.[37,110]

Titanium dioxide both in rutile and anatase form were identified in paintings and paints used by Sarmento because, both forms have very distinctive bands in the Raman spectrum: anatase at 640, 515, 395 and 145cm^{-1}; rutile at 610 and 450cm^{-1} [99] therefore it was relatively easy to distinguish them in the analyzed samples.

3.6.3.*Cenógrafa* Black: carbon black and iron black

Carbon black is the designation used for a group of well-defined, industrially manufactured products and 80 to 99.5 (wt%) of their chemical composition is made of carbon.[102] These blacks are renowned for their stability and their resistance to weathering is considered to be outstanding. Carbon blacks are used as polymer stabilizers, as they absorb visible, ultraviolet and infrared and also because they act as free-radical acceptors and inactivate intermediate species formed during polymer degradation.[102] For instance it is know that carbon black drastically reduces the oxidation rates of polychloprene a polymer very sensitive to photooxidation.[111]

Black iron oxide can be obtained from the mineral magnetite, or by precipitation. Either way it is chemical combination of ferrous and ferric oxides (Fe_3O_4). Iron oxide pigments are known for their hiding power, excellent light fastness and weather resistance.[1] As it is less black than the carbon blacks but are very cost effective [30] which might explain why the *Cenógrafa* black is made from a mixture of both.

[24] The stabilizing effect of rutile pigments is also significantly dependent on the manufacturing history of the pigment. [37] TiO_2 pigments can be produced by two methods: by hydrolysis of titanyl sulphate followed by calcination (sulphate process); and, by oxidation of titanium tetrachloride (chloride process). [102] The later can leave chlorine residues which can sensitize the photooxidation of the polymer. [37]

3.6.4.Calcium carbonate

Fillers are particles practically insoluble in the binding medium and are added to paints to improve technical properties and/or to influence optical properties.[25] [112] Their influence on coating materials properties can go from, dispersibility, packing density, paint spreading, hiding power, storage stability, reflectivity, mechanical properties to chemical resistance. Fillers refractive index is generally bellow 1.7 and since most binders have n_D<1.7 (for instance PVAc was a n_D of 1.5.[113]) it is expected that fillers do not contribute significantly to the hiding power of a dried film.[1]

Calcium carbonate is currently the dominant filler in paints and varnish industry.[112] Because it is a mineral compound with a low refractive index (n=1.63 [36]) when it is mixed with the pigments and the binding media it does not contribute to opacity and will simply act as a thickener. Being low in cost and being easily wettable by standard wetting agents and dispersants in aqueous paint systems, it is used to economically control application, rheological and the appearance characteristics of paints.

Surface's coating is a common practice and an organic coating material is usually used to eliminate the filler's hydrophilic character.[112] It prevents the formation of agglomerates during storage or to absorb the additives.[1] Stearic acid and its salts are used in large amounts to coat carbonate fillers.[1, 112] and may account for the vCH absorbance spectra of the carbonate used.

3.7.Surface analysis

Atomic Force Microscopy (AFM) imaging of the studied paint films done with the hompolymer emulsion *V7* shows an incompletely coalesced polymer film as polymer chain interdiffusion did not occur.(see Fig. I.7 and Table III.6) A similar honeycomb-type latex substructure has been seen in acrylic paint films.[36, 39, 80] Zumbül et al. report the incomplete coalescence of emulsion films and attributes it to additives. These were selectively marked with uranium and can been, after drying of acrylic latex, by SEM as they filled spaces between distinct and closely packed latex particles.[36] In PVAc emulsions another explanation is advanced by Keddie: the protective colloid PVAl has been found to form a continuous network that surrounds the PVAc latex particles decreasing the extent of coalescence.[34] Phase-imaging in AFM can give an indication of different materials present in samples because softer and harder regions are made visible.[114] As differences in contrast can suggest differences in chemical composition [114] of specific areas that might have given an indicating of the position of polymer particles and additives. Unfortunately, differences between the polymer particles and their boundaries could not be seen in any of the phase images obtained for these samples.

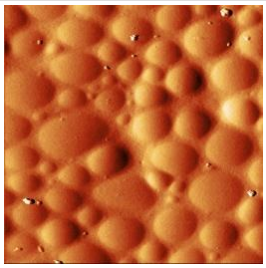
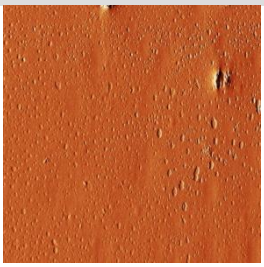
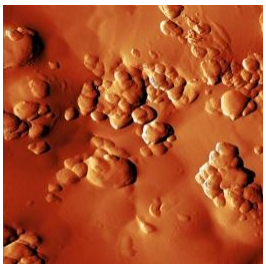
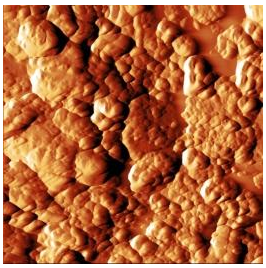
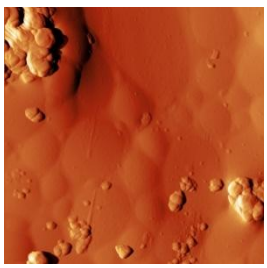
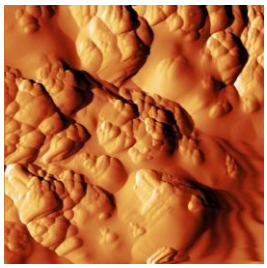
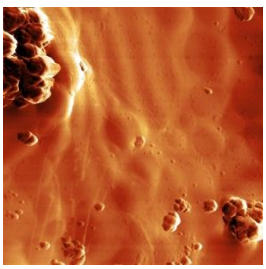
The film obtained with the P(VAc-E-VC) terpolymer shows a surface that is much smoother than the homopolymer film although it is covered with little flaws.

Amplitude images of pure white glue *V7* and *V7* plus dry pigments are somewhat different. In the first between polymer particles there is a smother surface that is not seen in the pigmented films.

[25] The definition is given according to the German Standards Institution, DIN 55943; the European Committee for Standardisation, EN 971-1; and, The International Organization for Standardization, ISO 3262. These standards are discouraging the use of terms like extenders.[112]

That can be related to the pigment's influence in film formation. For instance, research conducted by Hagan et al. suggest that the paint's surfactant is attracted to TiO_2 particles interface.[35] It is possible that a similar effect might have taken place and the surfactant is surrounding pigment agglomerates and not the polymer particles. What seems to be pigment agglomerates can be seen in the surface due to their poor dispersion in the emulsion. Pigment clusters produce higher surface roughness [115] hence the naturally higher Ra values for pigmented films.

Table III.6: AFM images from some of the studied binders and paint films

	***Vulcano V7* (PVAc hompolymer)**	***Vinamul 3469* (PVAc-E-VC terpolymer)**
Amplitude image		
	Ra: 23 ± 3	**Ra: 7 ± 2**
	***Vulcano V7* + *Cenógrafa* white** (laboratory mock-up)	***V7* + *Cenógrafa* white (artist's leftover)**
		
	Ra: 22 ± 3	**Ra: 125 ± 45**
	***V7* + *Cenógrafa* black** (laboratory mock-up)	***Bizonte* + *Cenógrafa* white (artist's mock-up)**
		
	Ra: 60 ± 18	**Ra: 68 ± 15**
Phase image		

3.8. Narrowing choices: formulation of the bindind media used by Sarmento

The main binder used by Sarmento in the 90's the white glue *V7* (later called *Bizonte*) had its composition changed at least three times. Analyzes of the emulsions show a PVAc homopolymer externally plasticized with DiBP and more recently a PVAc-VeoVa copolymer also externally plasticized with the same phthalate. However, analyzes conducted on Sarmento's paintings from the 90's (described in Chapter IV) show the presence of a PVAc hompolymer plastized with DBP. The change of the phthalate used is most probably related to wealth constrictions (as has been discussed in I.Introduction) imposed on the producers of the raw emulsion.

Regarding the *Sabu* paints three types of polymers were found: a PVAc homopolymer (on the pure binding medium), a PVAc-VeoVa copolymer (on coloured paints) and a P(VAc-E-VC) terpolymer (on the more recent formulation of the coloured paints). Some of the paints made with the copolymer were also externally plasticized with dibutyl phthalate.

The *Rowney* paints show a copolymer of P(VAc-E) with an aditional external plasticization achieved with DBP. An important remark should be made on the results obtained on the pure *Rowney* PVAc binding medium. The binding medium showed two distinct phases. A more fluid and transparent part and another more opaque and rigid one. The first revealed to be PVAc while the later showed the presence of PVAl. Therefore, this suggests that either the PVAc has hydrolyzed in some areas or, some phase separation ocured (PVAl is a common additive as it has been refered) leaving some areas richer in PVAl.

Although the infrared spectra of the paint samples was enough to distinguish some of the polymers present (the vinyl homopolymer from the terpolymer) others could only be distinguished by Py-GC/MS (the vinly homopolymer and the VeoVa copolymers). In most cases it seems that the presence of the phthalate made the spectra of both very similar. Moreover, it was found to be difficult to distinguish DiBP from DBP in the infrared spectra of the emulsions. A reliable identification could only be done with Py-GC/MS.

Imaging of the surface of some of the pure emulsions show that the type of polymer and/or the presence of additives influences the topography of the paint film. The homopolymer plasticized with a phthalate shows a honeycomb structure similar to what is found in other studies. Drying of the terpolymer emulsion resulted in a much smoother film. The ratio binder/pigment will naturally affect the surface. Laboratory reproductions of the homemade paints used by Sarmento (*Vulcano V7* with the *Cenógrafa* white) show a more regular surface when compared to paints prepared by the artist himself. It seemed that the later had a bigger binder loading.The results obtained and described in chapter II and III helped to narrow the choice of the materials to be tested: the homopolymer used in the *V7* (the main binder since the 90's), the terpolymer in order to ascertain the stability of the new formulations of the *Sabu* paints. As Sarmento works mainly with white and black since the 90's, these were the two colors chosen to be tested. It was essential to characterize the diferent polymers present in each emulsion to later be able to rational their aging behavior.

IV PVAc emulsions degradation: artificial aging studies

4.1. Accelerated aging conditions

In order to compare the photochemical stability of the homopolymer and the terpolymer paint reconstructions were subjected to accelerated aging.

For the conclusions to be applicable to the conservation field, conditions were chosen as to simulate as closely as possible the conditions a work of art is usually exposed to. As it has been mentioned photodegradation mechanisms are wavelength specific therefore samples were exposed to radiations similar to those encountered in museums where light is filtered by common window glass. Light that passes through ordinary window glass has a low content of wavelengths, below 310-315nm [58], therefore a high intensity Xenon-arc light source filtered to λ≥300nm was used. Irradiation was carried out at 800W/m^2 and five periods of aging were monitored 500h, 1750h, 3250h and a maximum of 4000h. Furthermore control unaged samples were studied.

According to Feller the annual radiation in a museum in London is 1.55% of the exterior therefore assuming that the average annual solar exposure is 3240MJ outdoors, the exposure indoors should be 50.22MJ.[58] As a result subjecting the samples to a total irradiance of 11294MJ/m^2 on 4000h of exposure ought to correspond to an exposure period of ≈225 years in a museum.

Black standard temperature was maintained at c. 50ºC and to diminish the effects of thermal degradation the temperature inside the chamber was cooled with an air conditioned apparatus.

4.2. Preparation of paint samples

Sarmento works mainly with white and black since the 90's therefore these were the two colours chosen to be tested. *Vulcano V7* and *Vinamul 3469* emulsions were used as binders. *Cenógrafa* white and black dry pigments were used because these are the representative pigments used in the 90's and titanium white rutile form because it is the pigment used nowadays. Both crystallines forms of titanium white were tested as TiO_2 is an important pigment in any contemporary artist *pallete*. As Sarmento can mix the binding medium and pigment more or less randomly, the proportion between binder, pigment and filler was chosen according to the proportion found on the *Sabu* paints (according to the company's formulation notebooks and a calibration curve calculated with FTIR).[26] (For detailed composition of the materials used see Table IV.1) Films of a wet thickness of 200μm were cast on ¼ of glass micro-slides. A uniform thickness was obtained by spreading the paint over the micro-slide using a film applicator (*Zehntner GmbH ZAF 2010*). Pure *Vulcano V7* and *Vinamul 3469* were studied both as casted films on micro-slides and on silicium disks. Poly(methyl methacrylate) reference films (20% w/v solution in acetone) were cast on micro-slides and on Si disks.

[26] At the time of the experience there was no knowledge that Sarmento used a specific binder/pigment ratio. After the artist provided that information his 'recipe' started to be used in the reconstructions.

Table IV.1 – Composition of the materials and paint formulations used to create the pigmented samples.

	Binding medium		Pigments			
Designation	*Vulcano V7*[#]	*Vinamul 3469*[#]	*Cenógraf* white*	*Cenógrafa b*lack*	Rutile*	Anatase*
Composition	PVAc homopolymer + DiBP + PVAl	P(VAc-VC-E) terpolymer•	$BaSO_4.ZnS$ + $CaCO_3$	Iron oxide + Carbon black + $CaCO_3$	TiO_2	TiO_2
	Ratio *binder*/pigment/filler (% weight)		***45*/ 30/ 25**	***45*/ 45/ 10**	***45*/ 55**	***45*/ 55**

As analyzed by µ-FTIR and Py-GC/MS
• Quantification by Py-GC/MS: 16%PVC. Comparing with reference spectra 15-20% of PE
*As analyzed by µ-FTIR; µ-Raman; µ-XRF

4.3. Results

4.3.1. Colour measurements (and gravimetry)

As expected a difference in color was observed for the *V7* which displayed a ΔE=4,14. However, *Vinamul* showed a much more significant change displaying a ΔE=47 (See Table IV.2 and Appendix IV. Artificial aging studies full results), due to the significant increase in b* values (yellowing). The pigments had a stabilizing effect on both polymers as the ΔE value is smaller than the value calculated for pure binders, being the effect higher with black pigments, for which no yellowing was observed in the *Vinamul* paints. *Vinamul* mixed with lithopone and calcium carbonate still shows a relevant yellowing displaying a ΔE=24.(See Fig. IV.1 and Table IV.2)

Also, no significant changes in weight were observed. Weight differences between the unaged samples and the aged samples are less than 2%. Yet, a remark should be made because in anatase containing samples with both binders the weight loss is superior than with the other pigments (≈2 to 1,5%).

Table IV.2: Colour coordinates and ΔE for the pure binders and for the mixture of the terpolymer and lithopone pigment over irradiation time.

	Homopolymer PVAc: V7			Terpolimer P(VAc-VC-E) Vinamul			Vinamul + Lithopone + $CaCO_3$		
	L*	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***
Unaged	89,6 ±0,06	-0,7 ±0,01	5,1 ±0,03	89,2 ±0,18	-1,0 ±0,01	4,8 ±0,03	90,0 ±0,04	-0,8 ±0,01	1,9 ±0,04
500h	89,1 ±0,62	-0,7 ±0,15	5,4 ±0,04	76,1 ±0,12	4,5 ±0,07	52,2 ±0,32	86,2 ±1,12	-1,1± 0,17	11,4 ±2,38
1750h	88,5 ±0,01	-1,5 ±0,01	9,6 ±0,07	71,0 ±0,17	8,0 ±0,14	55,7 ±0,41	73,9 ±0,12	4,0 ±0,03	19,9 ±0,02
3250h	89,2 ±0,08	-1,7 ±0,01	9,4 ±0,06	67,1 ±0,14	8,4 ±0,21	45,9 ±0,77	70,7 ±0,01	5,0 ±0,01	17,9 ±0,07
4000h	88,1 ±0,03	-1,3 ±0,01	8,9 ±0,03	68,4 ±0,52	8,4 ±0,69	49,9 ±3,16	73,0 ±0,02	4,0 ±0,01	17,9 ±0,02
Δ(L*, a*, b*)	**-1,5**	**-0,6**	**3,8**	**-22,0**	**1,2**	**41,0**	**-16,9**	**4,8**	**16**
ΔE		**4,1**			**46,6**			**23,7**	

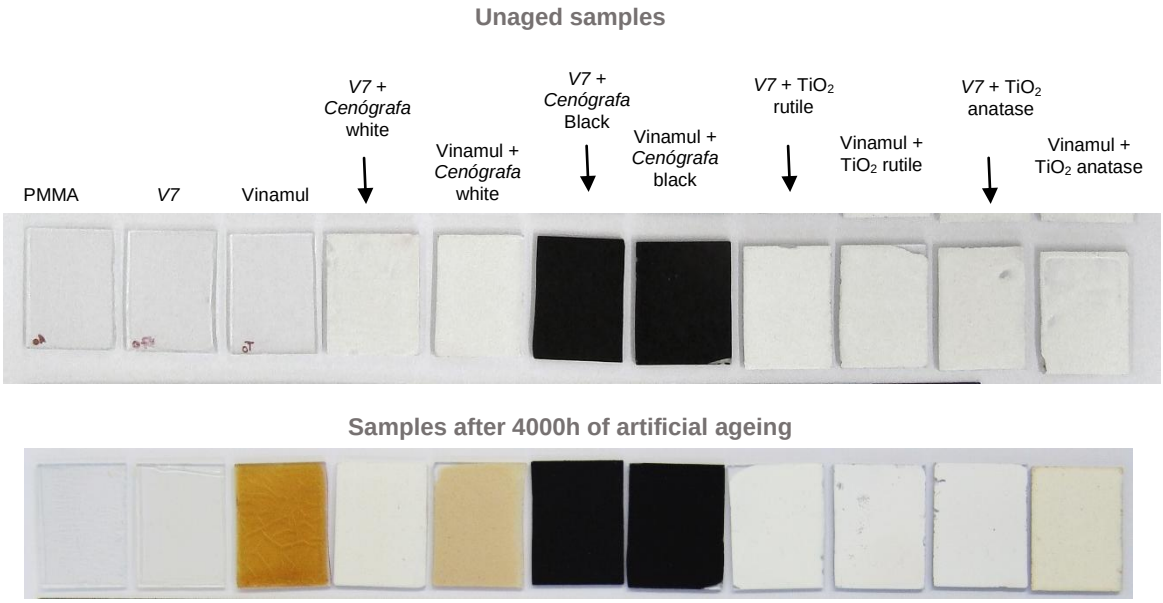


Fig. IV.1: Paint samples unaged (top) and after 4000h of accelerated aging (bottom).

4.3.2. GPC

None of the unaged binder and paint samples was found to be completely soluble in $CHCl_3$ from the start. (Table IV.3) Analysis of the gel portion revealed that a PVAc fraction was always insoluble in this solvent. Therefore it is not possible to verify if crosslinking is taking place in irradiated paint samples.

However, for pure *V7* the decrease of the insoluble fraction is in agreement with the expected chain scission.[6] Except for the lithopone containing sample all pigmented samples show a slight increase of the insoluble fraction. Regarding the measured Mw values in the soluble fraction for the pigmented samples only for samples containing anatase and litopone some diference could be found after 4000h of artificial aging. In the first case there is an increase while in the second there is a decrease of the Mw. Both carbon/iron black and rutile samples promoted a protective screening effect.

For the *Vinamul* P(VAc-VC-E) formulation the polymer is even more difficult to extract already at time 0 when compared to *Vulcano V7*.(Table IV.3) All samples except for the sample containing rutile show an increase in the insoluble fraction. Lithopone promoted crosslinking at the early stages of degradation i.e. at 500h. A significant fraction of the polymer grows insoluble and the signal obtained in the chromatograms is too weak to reliably calculate a M*w* value. For the soluble fraction in the other colored samples and pure binder, the main mechanism observed was scission, Table IV.4 and Fig. IV.2. However the diference in the Mw between unaged and aged samples is higher in the case of the unpigmented terpolymer emulsion. That indicates that regarding chain scission the pigment effect is protective, i.e., no photocalytic activity was observed, which may be attributed to an efficient competition for light by the pigment (screening effect).

Table IV.3: % of insoluble polymer in $CHCl_3$ for the pure binders and binders plus pigments through artificial aging.

% of insoluble polymer in $CHCl_3$					
	Unaged	**500h**	**1750h**	**3250h**	**4000h**
V7	36	35	40	13	25
+ Lithopone + $CaCO_3$	64	53	59	47	62
+ Fe_3O_4 + C + $CaCO_3$	22	45	37	42	34
+ TiO_2 rutile	38	53	27	60	-
+ TiO_2 anatase	25	14	22	30	28
Vinamul	61	66	68	74	77
+ Lithopone + $CaCO_3$	53	70	78	86	86
+ Fe_3O_4 + C + $CaCO_3$	53	50	53	52	61
+ TiO_2Rutilo	41	32	29	14	17
+ TiO_2 Anatase	32	47	48	43	65

Table IV.4: Average molecular weight (Mw) and polydispersity (PD) values of the soluble fraction over irradiation time.

	0h		**500h**		**1750h**		**3250h**		**4000h**	
	Mw (x10^3)	***PD***	**Mw (x10^3)**	***PD***	**Mw (x10^3)**	***PD***	**Mw (x10^3)**	***PD***	**Mw (x10^3)**	***PD***
PMMA	78	*1,5*	74	*1,6*	75	*1,8*	72	*1,8*	63	*2,0*
	Mw (x10^4)	***PD***	**Mw (x10^4)**	***PD***	**Mw (x10^4)**	***PD***	**Mw (x10^4)**	***PD***	**Mw (x10^4)**	***PD***
V7	45	*2,2*	42	*2,3*	33	*3,1*	20	*4,0*	23	*5,1*
+ Lithopone + $CaCO_3$	32	*3,5*	33	*3,8*	22	*4,3*	21	*3,5*	25	*5,3*
+ Fe_3O_4 + C + $CaCO_3$	40	*2,4*	45	*2,6*	40	*2,0*	34	*2,5*	40	*2,4*
+ TiO_2Rutilo	39	*2,4*	44	*2,7*	47	*2,4*	38	*2,7*	—[27]	
+ TiO_2 Anatase	36	*2,8*	43	*2,5*	43	*2,4*	40	*2,4*	44	*2,4*
	Mw (x10^3)	***PD***	**Mw (x10^3)**	***PD***	**Mw (x10^3)**	***PD***	**Mw (x10^3)**	***PD***	**Mw (x10^3)**	***PD***
Vinamul	30	*2,7*	24	*3,1*	15	*2,7*	9	*1,8*	8	*1,7*
+ Lithopone + $CaCO_3$	30	*3,0*	—	—	—	—	—	—	—	—
+ Fe_3O_4 + C + $CaCO_3$	30	*2,7*	31	*3,1*	32	*3,3*	22	*2,6*	28	*2,9*
+ TiO_2Rutilo	25	*3,0*	28	*2,6*	32	*3,3*	21	*2,7*	18	*2,4*
+ TiO_2 Anatase	31	*2,9*	15	*2,4*	23	*2,8*	28	*3,7*	22	*3,8*

[27] This samples were unfortunately contaminated while there were being used in a lecture for academic purposes. Therefore the results were useless for the research.

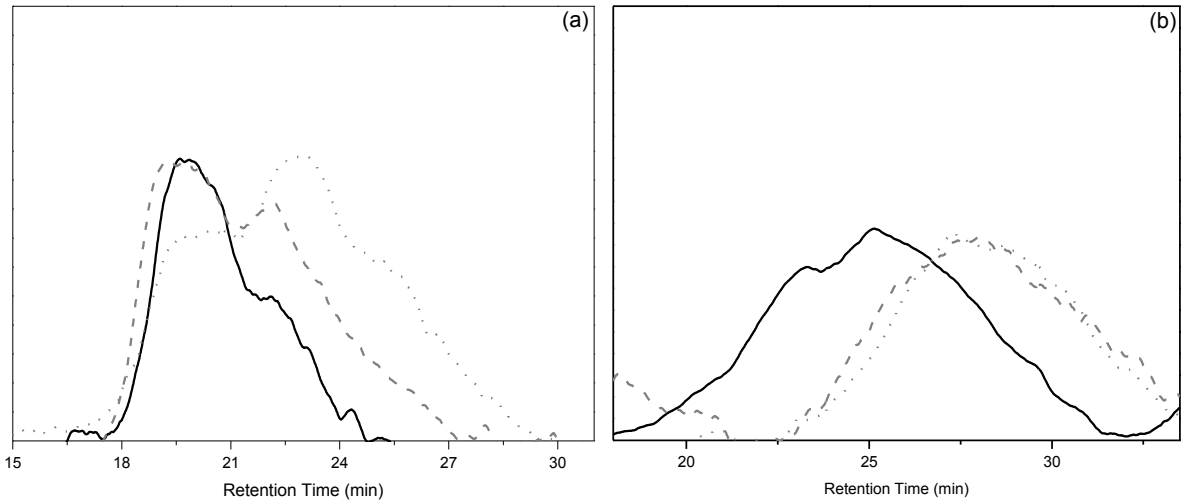


Figure IV.2: Molecular weight distribution over irradiation time for (a) *V7* and (b) *Vinamul*(—)0 h; (- - -) 1750h; (····) 4000h.

To compare the photostability of P(VAc-E-VC), PMMA and the PVAc homopolymer the number of scissions per chain ($S=Mn_0/Mn_t-1$) was calculated, Fig. IV.3 and Table IV.5. As expected, for P(VAc-E-VC) and PVAc the sequential decrease in M_W values and the slight increase in PD indicate that *V7* and *Vinamul* undergo chain-scission from the beginning of irradiation. It can be observed that PMMA displays the lowest rate of scissions per chain, followed by *Vinamu*l and *V7*. Considering the paint systems *V7* plus pigments over irradiation, an increase in M_W value for the initial irradiation times was detected, contrary to what was observed in our previous experiments.[6] This results of having developed a more efficient extraction system.

Table IV.5: Rate of scissions per chain: values for the slopes, *m*, and respective correlation coefficient, R^2, from the curves depicted in Figure 2.

	V7	***V7* +$BaSO_4$.ZnS + $CaCO_3$**	***Vinamul***	**PMMA**
m	9	2	3	1
R^2	0,97	0,75	0,94	0,9

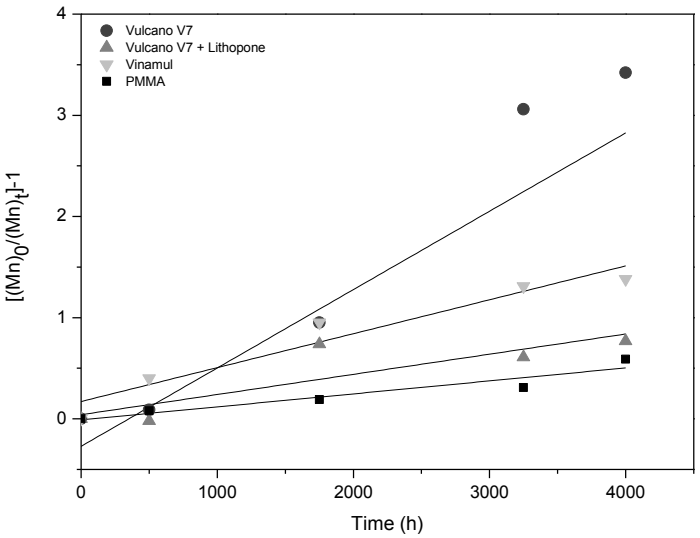


Fig. IV.3: *V7* and *Vinamul* rate of scission per chain as a function of irradiation time. Mn_0 = initial average molecular weight and Mn_t= average molecular weight after irradiation.

Considering the effect of Sarmento's pigments (*Cenógrafa* white and black and rutile titanium dioxide) on the photodegradation of *V7* it is possible to conclude that all promoted a stabilizing effect, less pronounced for the calcium carbonate plus lithopone mixture. For the later, although scission is observed, a decrease in its rate is observed when compared to pure *V7*, Fig.IV.3. For the other pigment formulations no significant decrease occurred with the M*w* over irradiation.

Pigments can act as protective absorbers by absorbing or, reflecting the damaging incident radiation and dissipating it harmlessly.[60] Therefore this protective effect may be explained if the pigment is able to compete for light absorption, without promoting any secondary photochemical reactions; the larger the fraction of light absorbed, especially for lower wavelengths, the more efficient this effect will be. Fig. IV.4. presents the reflectance spectra of the two whites studied. Rutile titanium dioxide reflects visible light and starts absorbing at c.426nm e.g. it cuts off radiation below 400 nm and is possibly encapsulated, therefore a strong protective effect is observed. Cenógrafa white shows a similar behavior except it starts absorbing at slightly lower wavelengths c.412nm. This absorption ends around 256nm. There is absorption between 790-650nm with a maximum peak at 733nm. This composite absorbance band between 650-750nm is attributed to the cobalt ion (used has was mentioned to stabilize the pigment) coordinated with the sulphur in ZnS.[105] According to literature values ZnS starts absorbing at c.346nm until 275nm with a small shoulder at c.240nm. In fact zinc sulphide's absorption in the near ultraviolet range is usually used for UV curing of polymers[28].[1;102]

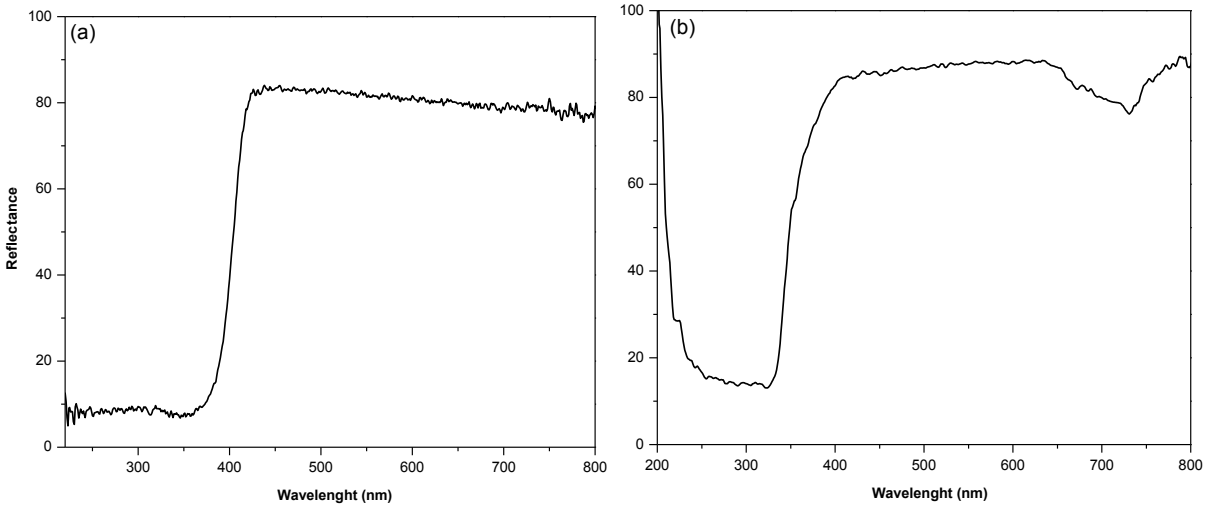


Fig. IV.4: Reflectance spectra of (a) rutile titanium dioxide and (b) *Cenógrafa* white (lithopone + calcium carbonate)

4.3.3. Infrared spectroscopy

Vinamul

The infrared spectra of P(E-VC-VAc) is dominated by the PVAc fingerprint and the relevant absorptions by C-Cl (bending at 1330cm^{-1} and 1251cm^{-1}) are overlapped by the ester bands. This is in agreement with 60-70% of PVAc in the terpolymer and with the lower molar absorption coefficients for the C-Cl bending and stretching when compared with the C=O or C-O absorptions.

[28] The term curing is occasionally used to designate cross-linking of a polymer, linking the polymer chains together through covalent or ionic bonds to form a network.[11]

Taking into account the observed yellowing we anticipated that the formation of polyenes would competing with photo-oxidation. In PVC systems a competition between the formation of polyenes and their "bleaching" by photooxidation is in favor of the first due to their much higher extinction coefficient as described before.[47] (Fig. IV.8) As a consequence they compete efficiently for light absorption, inhibiting the absorption of light by other chromophores as hydroperoxides, ketones and other oxygenated functional groups. Therefore we might anticipate that, for our ageing conditions, no relevant changes in the carbonyl functions are expected. However both the pure P(VAc-E-VC) sample and P(VAc-E-VC) plus pigments show changes in different regions of the infrared spectrum due to the formation of oxidized species. The changes are more noticeable in the pure binder and when it is pigmented with the $ZnS.BaSO_4$ and $CaCO_3$ mixture.

The appearance of a broad band due to νOH at c. 3443cm^{-1} in the pigmented sample and at c. 3456cm^{-1} in the pure binder may be attributed to hydroxyl functions. This absorption has also been detected by other authors [42-44, 48, 50, 73] and has been assigned to hydroperoxides [48]. It should be referred that the formation of hydroperoxides has also been detected in the infrared spectra of pure PVAc although the irradiation was in the ultraviolet region.[69] And that in fact there is an increase in the formation efficiency of these photoproducts in PVC/PVAc blends when compared to PVC alone. [73]

Changes in the carbonyl region show the appearance of oxidized groups in all the samples except for the ones containing black pigment. Quantification of the carbonyl absorption band before and after aging reveals that the initial width at half maximum (σ) of the νC=O of the pure binder increases by ≈19%, samples with rutile show an increase of ≈17%, and samples containing anatase increased by ≈21%. The observed ability of rutile TiO_2 to decrease the oxidation rate of PVC, while anatase TiO_2 shows higher photoactivity towards the polymer as also been seen by Kemp.[117] The paint samples containing lithopone show noticeable changes with a considerable broadening as the σ value goes from ≈24 to ≈65 and moreover the νC=O shifts to lower wavenumbers.(see Table III.8) The νC=O is now centered at 1720cm^{-1} due to the appearance of a shoulder at c.1713cm^{-1}. The appearance and predominance of a C=O absorption at c.1715cm-20cm^{-1} is eminent in several PVC photodegradation studies [42-44, 48, 50-53, 73] and has been assigned to the formation of chlorocarboxylic acids.[48]

Kaczmarek observed that in blends of PVC and PVAc exposed to UV-irradiation there is abstraction of side ester groups and this reaction could be attributed to the formation of the chlorine radical that evolves from PVC.[73] This radical can abstract the hydrogen from PVAc, forming the acetate radical that leads to the deacetylation of PVAc. [116] IN the present case the analysis of the C-O region is not straightforward due to the fillers absorption between 1500-900cm^{-1}. Therefore it is not possible to ascertain if there is disappearance of the acetate group.

In pigmented samples in the νCH stretching region the νCH (CH_2) absorption at 2933-35cm^{-1} decreases (See table IV.6) and the νCH(CH_3) absorption goes from 2860-63cm^{-1} to 2874cm^{-1}. The decrease of these absorptions has also been noted by Kaczmarek for blends of PVC and PVAc exposed to UV-irradiation and were attributed by the author to chain degradation [73]. Absorbance ratios of the νC=O also decrease significantly in samples containing lithopone.

Although the appearance of polyenic sequences was expected due to the yellowing of the samples none of its characteristic absorptions was detected in the infrared spectra either because they were formed in very low concentrations [48] or due to their low absorption values.

Table IV.6: Relative intensity of the main infrared absorptions in the infrared spectra of the terpolymer *Vinamul* Before and after 4000h of artificial agin. Infrared spectra were baseline corrected and normalized for the C=O stretching.

	νC-H	***νC=O***	***νC-O (CO)O***
	2934-36	**1733-36**	**1233-42**
Vinamul unaged	—	1,00	0,96 ± 0,07
Vinamul aged	—	*1,00*	*0,86 ± 0,11*
***Vinamul*+ lithopone unaged**	0,15 ± 0,00	1,00	0,92 ± 0,03
Vinamul+ lithopone aged	*0,12 ± 0,01*	*1,00*	*1,21 ± 0,14*
***Vinamul*+ black unaged**	0,14 ± 0,01	1,00	0,79 ± 0,03
Vinamul+ black aged	*0,12 ± 0,00*	*1,00*	*0,74 ± 0,01*
***Vinamul*+ TiO_2 rutile unaged**	0,13 ± 0,01	1,00	0,77 ± 0,03
Vinamul+ TiO_2 rutile aged	*0,10 ± 0,02*	*1,00*	*0,76 ± 0,00*
***Vinamul*+ TiO_2 anatase unaged**	—	1,00	0,81 ± 0,01
Vinamul+ TiO_2 anatase aged	—	*1,00*	*0,79 ± 0,07*

Vulcano V7

The only change observed in the infrared spectra of *V7* (Fig. IV.5), as previously reported, [6] is the loss of the phthalate. Its disappearance of this plasticizer from the pure binder can be monitored by looking at the νCH stretching bands at c.2935 and 2876cm^{-1}, the δ(ring-H) at 1123cm^{-1} and the ν_{as}(C-O-CO) at 1073cm^{-1} as these absorbance bands are mainly due to the phthalate. Decrease of the relative intensity of these absorptions to the C=O stretching is shown in Table IV.7.

In the infrared spectra of *V7* mixed with lithopone, rutile and black pigment the νC-H shifts to slightly higher wavernumbers reflecting the disappearance of the phthalate plasticizer and the dominance of PVAc characteristic values. Absorbance ratios could only be calculated within an acceptable experimental error for lithopone and rutile samples. However the FTIR spectra show that loss of DiBP is more severe in some areas of the samples containing anatase as the band at 2874-77cm^{-1} and the band at 1073-75 cm^{-1} disappears. None of the samples suffered a significant

change in the area or shape of the νC=O absorption peak. The difference between the unaged and aged samples falls beneath 10%.(See Table IV.8)

Table IV.7: Relative intensity of the main infrared absorptions in the infrared spectra of the *V7* homopolymer before and after 4000h of artificial aging. Infrared spectra were baseline corrected and normalized for the C=O stretching. Values are the average of three different areas of the same sample.

	νC-H			***νC=O***	***δC-H (CH_2)***	***δ C-H(CH_3)***	***ν C-O (CO)O***	***δ (ring-H)***	***ν C-O (C-O-CO)***	***ν C-O O(CH)***
	2965	**2937**	**2876**	**1736**	**1432**	**1373**	**1241**	**1123**	**1073**	**1022**
***V7* unaged**	0,09 ±0,01	0,08 ±0,01	0,03 ±0,00	1,00	0,09 ±0,01	0,34 ±0,05	0,81 ±0,07	0,20 ±0,04	0,17 ±0,03	0,27 ±0,04
V7 aged	*0,07 ±0,02*	*0,06 ±0,01*	*0,02 ±0,00*	*1,00*	*0,08 ±0,01*	*0,31 ±0,06*	*0,75 ±0,11*	*0,16 ±0,03*	*0,13 ±0,03*	*0,24 ±0,06*
***V7* + litopone unaged**	0,09 ±0,02	0,07 ±0,02	—	1,00	—	—	—	—	—	0,24 ±0,04
V7* + *litopone aged	*0,07 ±0,02*	*0,06 ±0,02*	—	*1,00*	—	—	—	—	—	*0,26 ±0,02*
***V7* + rutile unaged**	0,07 ±0,00	0,06 ±0,00	—	1,00	0,06 ±0,00	0,28 ±0,01	0,71 ±0,02	0,13 ±0,01	0,11 ±0,01	0,18 ±0,01
V7* + *rutile aged	*0,05 ±0,01*	*0,05 ±0,01*	—	*1,00*	*0,09 ±0,01*	*0,30 ±0,02*	*0,70 ±0,01*	*0,13 ±0,01*	*0,11 ±0,01*	*0,20 ±0,01*

Table IV.8: Values of peak centre (μ), full width at half maximum (σ) and area (A) calculated by fitting the νC=O absorption with a Gaussian function before and after artificial aging. The values are the average of three infrared spectra taken from each sample. Spectra were baseline corrected and normalized by the intensity of the carbonyl absorption band.

	μ		**σ**		**A**	
	0h	*4000h*	0h	*4000h*	0h	*4000h*
Vinamul	1734	*1734*	28,12	*33,50*	29,08	*29,38*
***Vinamul*+ lithopone**	1737	*1720*	23,89	*64,59*	24,57	*69,92*
***Vinamul*+black**	1736	*1736*	22,82	*22,75*	23,53	*22,75*
***Vinamul*+rutile**	1738	*1737*	22,54	*26,46*	23,55	*26,49*
***Vinamul*+anatase**	1737	*1738*	23,11	*27,86*	24,07	*27,51*
V7	1736	*1736*	27,33	*24,85*	27,88	*26,37*
***V7* + lithopone**	1738	*1738*	25,18	*24,29*	26,23	*25,38*
***V7* + black**	1737	*1738*	25,55	*23,36*	25,03	*24,64*
***V7* + rutile**	1738	*1739*	24,34	*23,77*	25,29	*24,63*
***V7* + anatase**	1738	*1739*	25,56	*27,28*	26,55	*28,91*

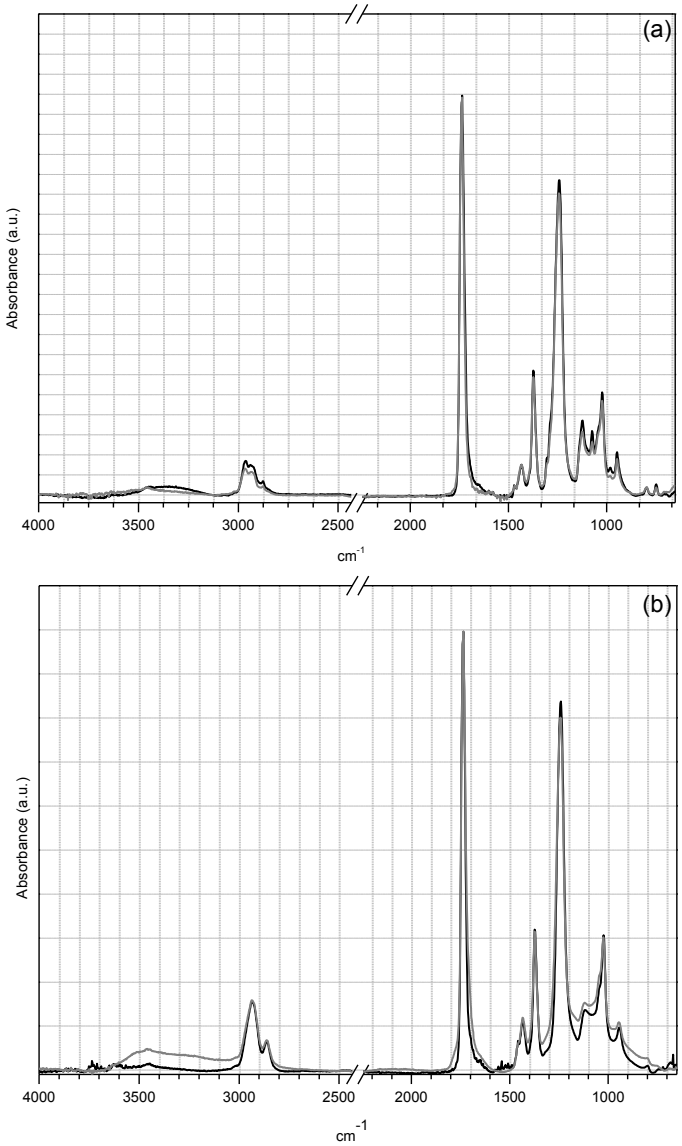


Figure IV.5: Infrared spectra of the (a) *V7* PVAc and (b) *Vinamul P*(VAc-E-VC) emulsions through artificial aging: (—)0 h; (—) 4000h.

4.3.4. Py-GC/MS

The pyrogram of the unaged *V7* (Fig.III.2) contains the PVAc characteristics peaks [2]. Acetic acid elutes at ≈2:70min and the mass spectrum shows the characteristic m/z values at 60 and 43. Benzene elutes at ≈ 2:76min and the mass spectrum contains the characteristic m/z values at 78 and 51. The peak eluting at higher retention times ≈12:32min corresponds to the plasticizer. The mass spectrum of this peak shows the characteristic m/z values for the DiBP at 149, 223, 57, 104. Py-GC/MS analysis conducted on the aged *V7* pure emulsion and this binder plus white pigment lithopone revealed that DiBP might be degrading. (Fig. IV. 6) Another phthalate of higher molecular height eluting at ≈ 12:90min and with a mass spectrum with m/z values of 149, 55 and 202 appears in the pyrograms of the irradiated samples. Also for both samples (pure *V7* and *V7* plus

white pigment) the difference between unaged and aged chromatograms obtained with the pyrolysis is the appearance of a peak that corresponds to phthalic acid or, phthalic acid anhydride. This compound elutes at ≈9:00min and the mass spectrum shows m/z peaks at 104, 76, 50 and 148.(Figs.IV.7) Because they have equal mass spectra they cannot be distinguished.

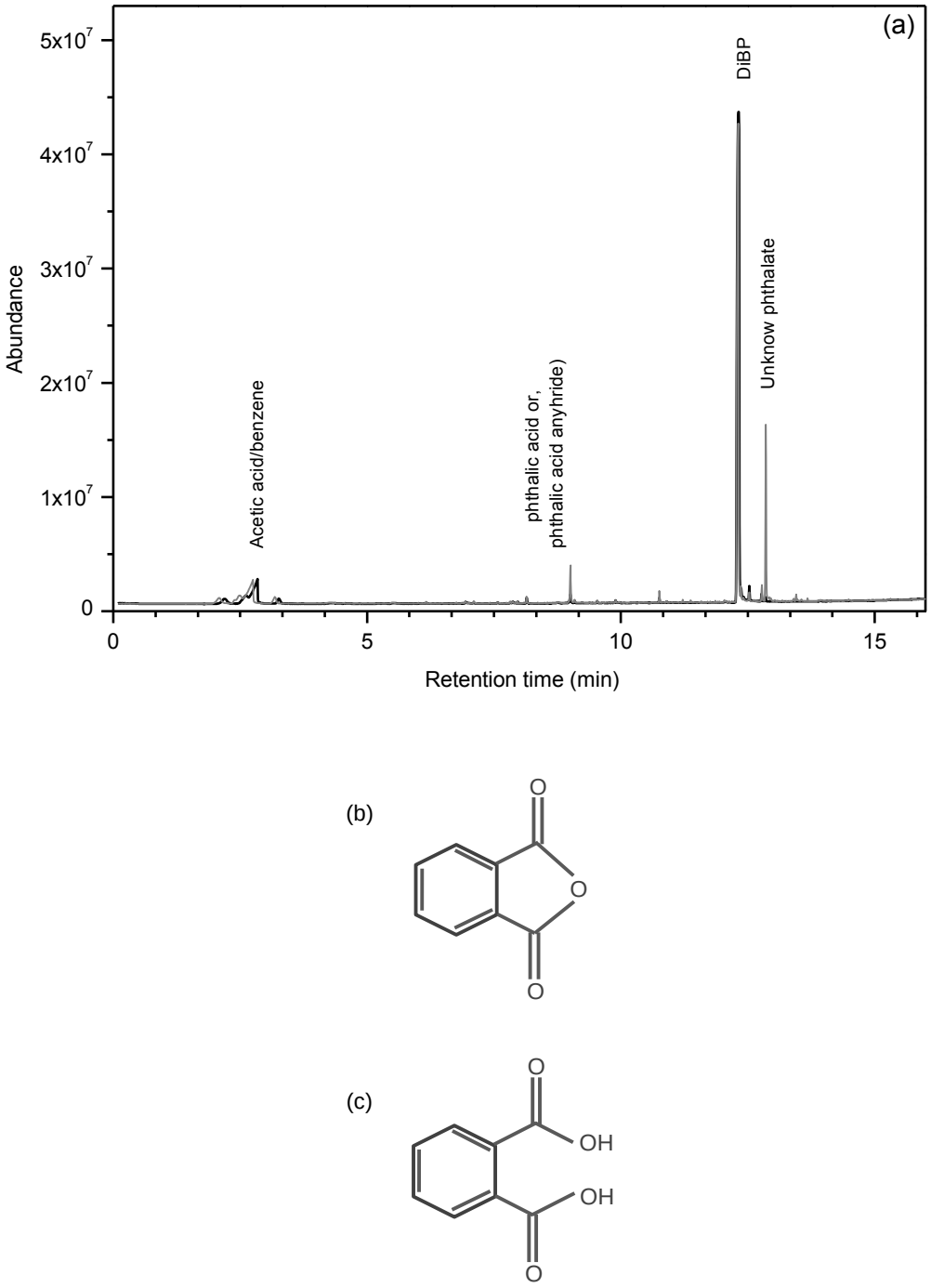


Fig. IV.6 – (a) Total ion count pyrogram obtained with pyrolysis at 550ºC for the sample *V7* plus lithopone before aging (—) and after aging (—). (b) Structure of phthalic acid anhydride and (c) of phthalic acid.

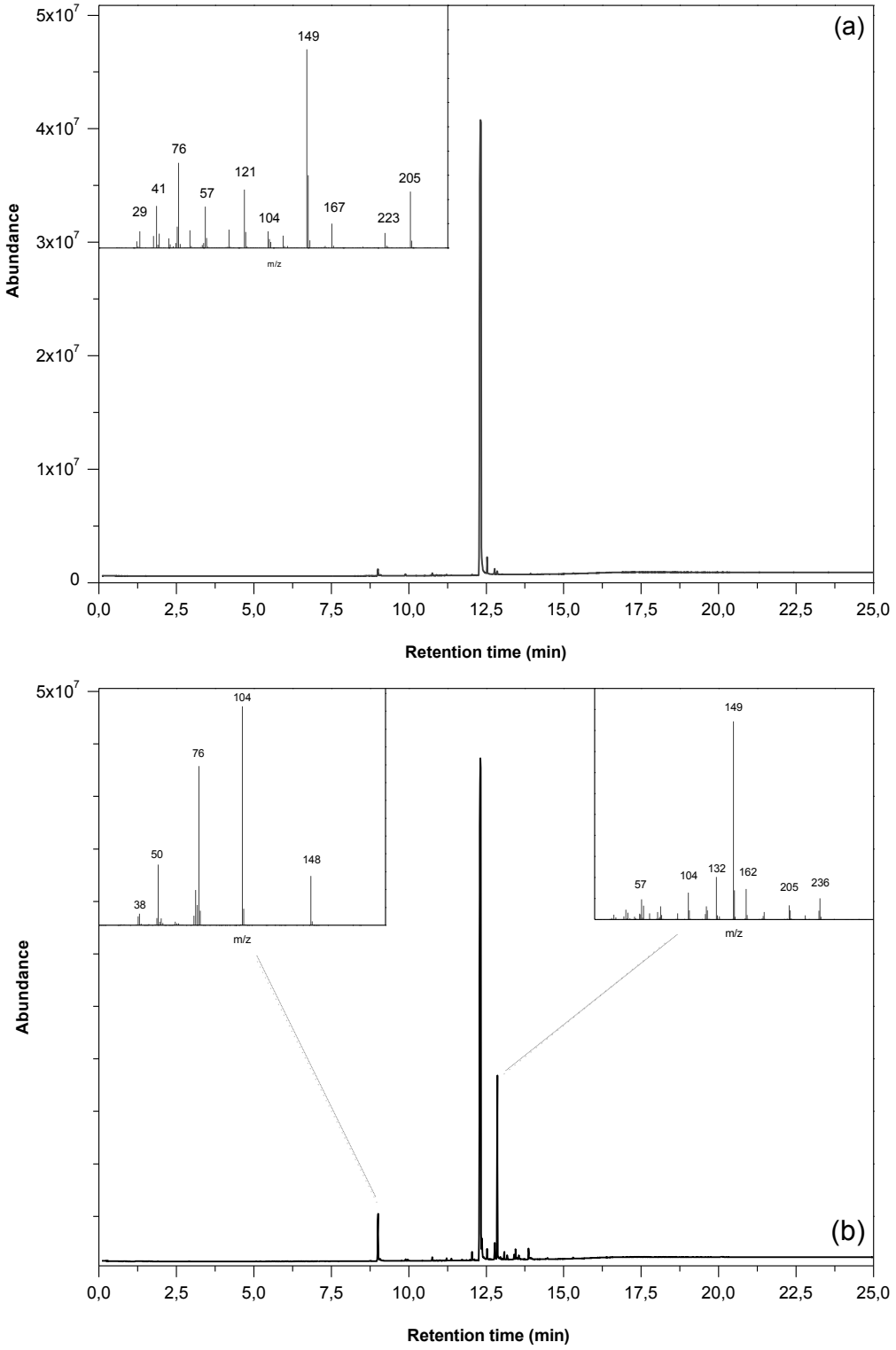


Fig. IV.7 - Pyrograms from the temperature-resolved additive fractions (pyrolysis at 100ºC-225ºC) from pure *V7* before (a) and after artificial aging (b). Inset mass-spectrums presented in (a) are from the DiBP and in (b) from the phthalic acid anhydride or, phthalic acid (left) and from an unidentified phthalate (right).

Detection of phthalic acid correlates well with the current knowledge on phthalate degradation. Environmental degradation of phthalates can occur by hydrolysis, photodegradation and biodegradation.[118] Hydrolyzes occurs when the phthalate is exposed to strongly acidic or alkaline conditions and produces following two hydrolytic steps: first the mono-ester and one free alcohol moiety; and, a second hydrolytic step creating crystalline phthalic acid and a second alcohol.[23, 27] However hydrolysis is unlikely to be an important fate for phthalate esters under typical environmental conditions because they occur at extremely slow rates and photodegradation via free radical attack is expected to be the dominant degradation pathway in the atmosphere.[27, 118] Photodegradation occurs by reaction with hydroxyl radicals and half life calculations show that these reactions are important regarding the fate of phthalates in atmosphere. Measured values of half-lives for DBP and DiBP are the same: 0,6-6 days.[27] If one considers the pH of the studied glues in liquid state (see Table IV.9) hydrolytic reactions might be considered. However the pH values measured in the surface of a 20 year old white paint done with PVAc containing dibutyl phthalate and *Cenógrafa* white shows the paint has a neutral pH (6,7±0,1, p.128). Therefore plasticizer photodegradation is what is most probably occurring.

Table IV.9: pH values taken of the studied glues in a liquid state.
The values are the average of three measures.

Sample	*Vulcano V7*	*Sabu* tempera acrilica	Painting surface
pH	3.31±0.01	5.51±0.01	6.65±0.14

Besides showing the plasticizer degradation Py-GC/MS also showed differences between the *V7* and the pigmented white sample. In the later desorption released not only the plasticizer but, also some acetic acid and benzene. That can be correlated with the chain scission observed in GPC. Formation of shorter polymer chains may help in to their release at lower temperatures. In the case of the pure emulsion the pyrogram between 100-225ºC only contains plasticizer.(see appendix IV)

4.3.5. Surface studies: AFM

The effects of artificial aging were followed by Atomic Force Microscopy, in the tapping mode, on areas of 2x2µm^2, 10x10µm^2 and 50x50µm^2. In Table IV.10 representative images from the 10x10µm^2 areas are showed. Analyses were performed in the *V7* and *Vinamul* pure samples. As it was already described the surface of the two emulsions was very different. *V7* displays an uneven surface where the polymer particles did not coalesce completely upon drying. *Vinamul* displays a regular surface with small holes dispersed heterogeneously across the surface. Regarding the behavior with aging, in the case of the homopolymer the topography of the samples and the roughness values (Ra) did not change significantly after 4000h of artificial aging. However in case of the terpolymer there are more holes in the surface which explains the significant increase in the Ra values. Although a direct correlation with the chemical changes observed with other techniques

cannot be made it should be stressed that the terpolymer did show higher photo-instability namely, formation of oxidation productions and yellowing.

In the pigmented samples it is worth to mention that the homopolymer and *Cenógrafa* white (the most used pigment by Sarmento) after aging exhibited a significant decrease (<30%) in the Ra values when compared to the *Cenógrafa* black. (Table IV.11) This is in agreement with the analyzes (namely, GPC and Py-GC/MS) described previously were it is showed that lithopone plus the hompolymer is less stable than with the black pigment. Taking into account the results of the other analyzes

Table IV.10 - AFM images of the pure binders before and after artificial aging. Height images are displayed on the left and amplitude images on the right for each sample. *Ra* was calculated on the 10x10μm^2 scan areas as an average of five selected 2x2 μm^2; the average value presented is the average of the results of each samples.

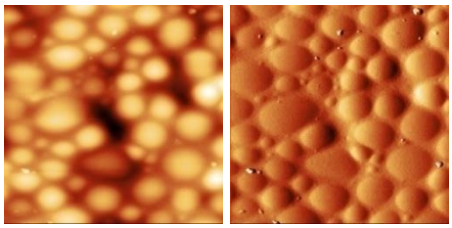
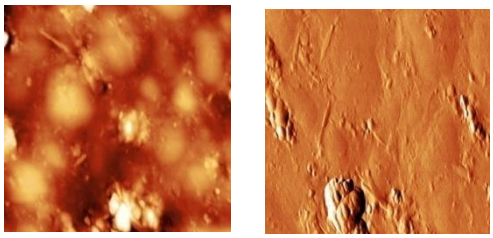
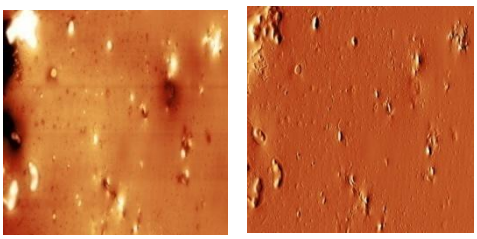
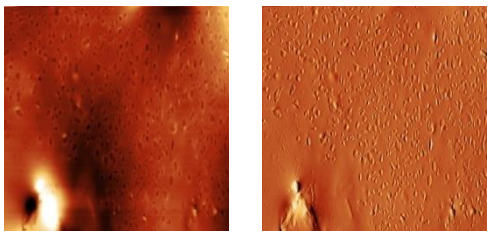
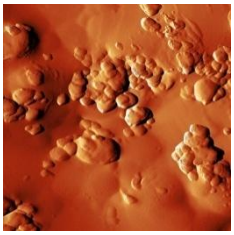
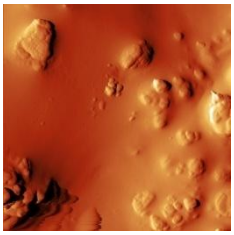
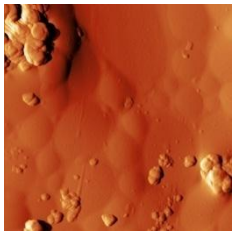
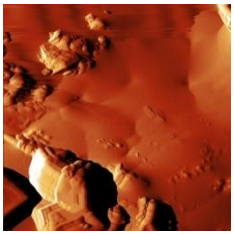
***Vulcano V7* (PVAc hompolymer)**	
Unaged	Aged 4000h
	
Ra (nm) = 20±3	**Ra (nm) = 22±3**
***Vinamul 3469* (P(VAc-E-VC))**	
Unaged	Aged 4000h
	
Ra (nm) = 7±3	**Ra (nm) = 17±3**

Table IV.11 - AFM images of the colored paint reproductions before and after artificial aging. Height images are displayed on the left and amplitude images on the right for each sample. *Ra* was calculated on the 10x10μm^2 scan areas as an average of five selected 2x2 μm^2; the average value presented is the average of the results of each samples.

***V7* + *Cenógrafa* white**		***V7* + *Cenógrafa* black**	
Unaged	Aged	Unaged	Aged
			
Ra (nm) = 483±90	**Ra (nm) = 327±68**	**Ra (nm) = 316±73**	**Ra (nm) = 326±68**

4.3.6. DSC analyzes

For the DSC analysis (Table IV.12) the following remarks should be made. All the pure polymers suffer an increase in the Tg with artificial aging. The pure homopolymer, *Vulcano V7* presents a higher increase when compared to the others. This increase may be due to the loss or, degradation of the plasticizer as can be seen in the Py-GC/MS.

It´s interesting to notice that the Tg of a white paint sample naturally aged (included here for comparision purposes) is close to the value of the *V7* + lithopone unaged (laboratory reproduction) but, higher than the value obtained for the unaged pure polymer (*Vulcano V7*)

Table IV.12 – Summary of results obtained with DSC analysis.

Sample	Polymer +additive	Results
Vinamul unaged	P(VAc-E-VC)	15.2 ºC
Vinamul aged	*P(VAc-E-VC)*	*18.2 ºC*
***V7* unaged**	PVAc + DiBP	10.2 ºC
V7 aged	*PVAc + DiBP + phthalate*	*20.0 ºC*
***V7* + lithopone unaged**	PVAc + DiBP	16.2 ºC
V7 + lithopone aged	*PVAc + DiBP + phthalate*	*21.4 ºC*
White paint sample from the 90's	PVAc + Dibutylphthalate	14.9 ºC

4.4. Conclusions

As expected the emulsion based on the terpolymer is less stable than the emulsion formulation based on the homopolymer. The results are in agreement with the aging behavior described in the literature (See 1.3.4. Poly(vinyl chloride) photodegradation). There was a noticeable yellowing of

the film; infrared revealed the formation of oxidized species; GPC showed the occurrence of chain scission but, the increase of the insoluble gel suggests that cross-linking might also be occuring. These results raise awareness that further testing should be made in the modern colored *Sabu*s because these paints continued to be used by artists until its production cessed not so long ago.

The homopolymer based emulsion proved to be more stable, yellowing less and the GPC analysis indicated that chain scission is the main process occurring. Py-GC/MS analyzes also support the chain scission seen in the GPC analyzes. No significant molecular changes were observed in the infrared spectra. Only the loss of the phthalate was deteted. Quantification made with Py-GC/MS showed that from the initial 21% of plasticizer 14% (DiBP plus degraded phthalate) remain in the film.

Overall the changes in the paint properties studied of the pure emulsions were also detected when the mixture lithopone+calcium carbonate is present in the samples. Mixed with the terpolymer, lithopone + calcium carbonate did not help to stabilize the polymer significantly. Yellowing of the emulsion decreased but not significantly. It promoted further degradation of the polymer as it promoted crosslinking in an early stage of irradiation. And the infrared showed the formation of degradation products (namely hydroperoxides and other oxidation species). In the case of the homopolymer a slight stabilization of the polymer is produced when used with the *Cenógrafa* white. There is a negligible degree of yellowing (ΔE=1.53) even less yellowing than the pure *V7*. The rate of chain scission is lower than when compared with the pure emulsion. However there is also a less pronounced stabilizing effect as the rate of chain scission in this paint sample is higher than when other pigments are present.

Moreover the Py-GC/MS analysis revealed that the DiBP is photodegrading. This effect was found in the aged pure film of *V7* and in the colored sample containing *Cenógrafa* white. Taking into account that this occurs in both samples and that the *V7* showed less topography changes than when it is mixed with the *Cenógrafa* white this process may account for the lack of a surface enrichment of this additive. Presumably the additive may migrate to the surface where it is degraded by light and oxygen. The degradation of the phthalate may also account for the increase of the emulsion and of the paint's Tg with aging.

With the results obtained on the laboratory reproductions subjected to accelerate aging a comprehensive view and knowledge of these material's molecular changes could be set. This was then compared with the analysis done on case-studies as natural aged paints. The results on artificial aging sugest that the studied paint properties change especially when the mixture lithopone plus calcium carbonate is present in the samples. This means that this pigment does not have a stabilizing effect which causes concern over the preservation of Sarmento's works as this pigment was extensively used by the artist since the 90's. And although artificial aging namely in what regards the yellowing of the white paints does not seem to correlate with the values measured in the paintings from the 90's the yellowing of the pure emulsion does seem to correlate with the yellowing observed in some enriched binder areas on some of the studied paintings. Works done more recently that contain rutile TiO_2 are expected to be more stable as this pigment showed to have a strong stabilizing effect on the polymer.

V. Case studies and conservation state

In terms of the materials identified the differences encountered in the 11 paintings studied are related to the type of vinyl polymer (co or homopolymer) and the additives added by the producer in the emulsion formulation. Besides even when only a type of binder and one type of dry pigment is used the ratio between binder and pigment is uneven as Sarmento's seeks different textural effects.

Results obtained during accelerated aging were used to assess the conservation state of the selected Sarmento's paintings. Visual examination of works from the 80's reveals that they are in good condition as no loss of cohesion or of adhesion was detected. On the other hand paintings from the 90's show a pronounced discoloration (yellowing). Therefore in the following description of the painting's condition and analytical results a special emphasis is given on the *White Painting* series due to the apparent degradation problems. A summary of the results is presented in Table V.1 and full results on the characterization and conservation state are compiled in Appendix V: Case studies full results.

5.1 Paintings from the 80's

Salto and *52 (cinquenta e dois quadros para 2000) (Figs. II.10 and II.11)* are characterized by strong colors that fill the background and/or delineate figures with sketchy brushstrokes. Paintings from the first half of this decade are usually more flat in texture. Latter more textured and prominent masses and strokes of paint are preferred.(See Figs. V.1 and V.2) Works painted over paper display deformations which are related to the paper's reaction to the emulsion's water when paint is applied. *Salto* was painted over paper and does not exhibit any of these deformations because it was glued to a stretched canvas. This procedure was a later addition without the artist's knowledge. *52* was painted over canvas and different painterly effects were also attained by gluing pieces of paper and newspaper over the textile support.

The smooth surface and regular colors of *Salto* contrast with the highly textured surface and uneven colours of *52*.

Infrared and Py-GC/MS analyzes from S*alto* showed that at least two of the colors analyzed are PVAc-VeoVa based emulsions with diethyl phthalate added as an external emulsifier.(Figs. V.3 – V5) Infrared spectra from the remaining colors are not straightforward as the paint layers are more or, less impregnated with the chloroprene glue used to attach the paper support to the canvas. For instance one can only say that in the blue and black colors a PVAc based polymer was used taking into account the C=O stretching at 1741-35cm^{-1} and the CO stretching from the ester group at 1244-41cm^{-1}.

Infrared analyzes from *52* show a PVAc based binder in all the colours analyzed. As for the white pigments used both forms of TiO_2 (anatase and rutile) (Fig. V.5) were detected as well as lithopone.

Fig. V.1 and V. 2: Details from *Salto* (left) and *52* (right)

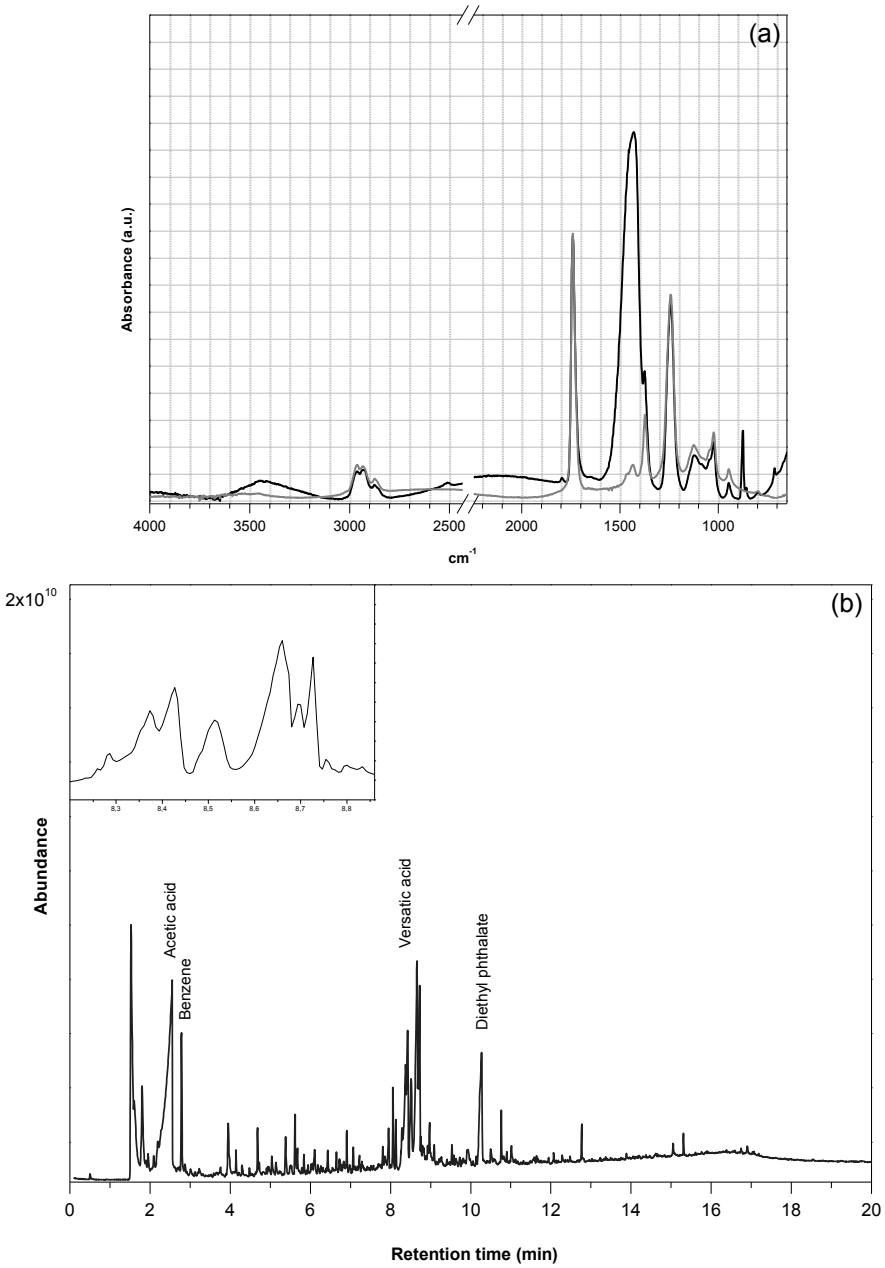


Fig. V.3: (a) Infrared spectrum of the PVAc-VeoVa binder in the red paint layer from *Salto*. (b) Pyrogram from the white paint sample showing a PVAc-VeoVa copolymer (the characteristic peaks are show in the pyrogram's inlay)

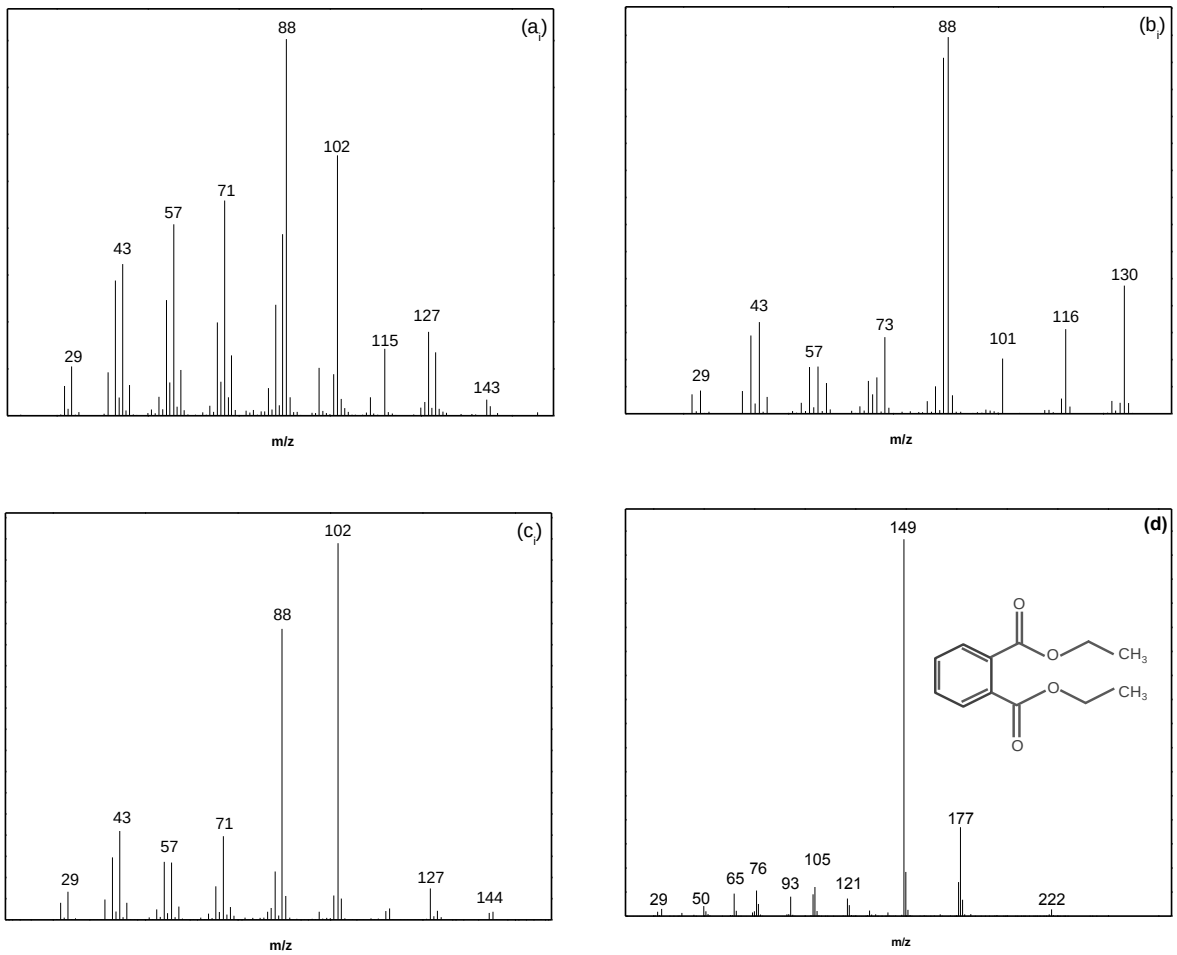


Fig. V.4: (a_1, b_1 c_1) Mass spectrum of the VeoVa component present in the binder of the white paint layer and shown in inlay of Fig. V.3 (d) Mass spectrum from DEP (peak eluting at 10:77min)

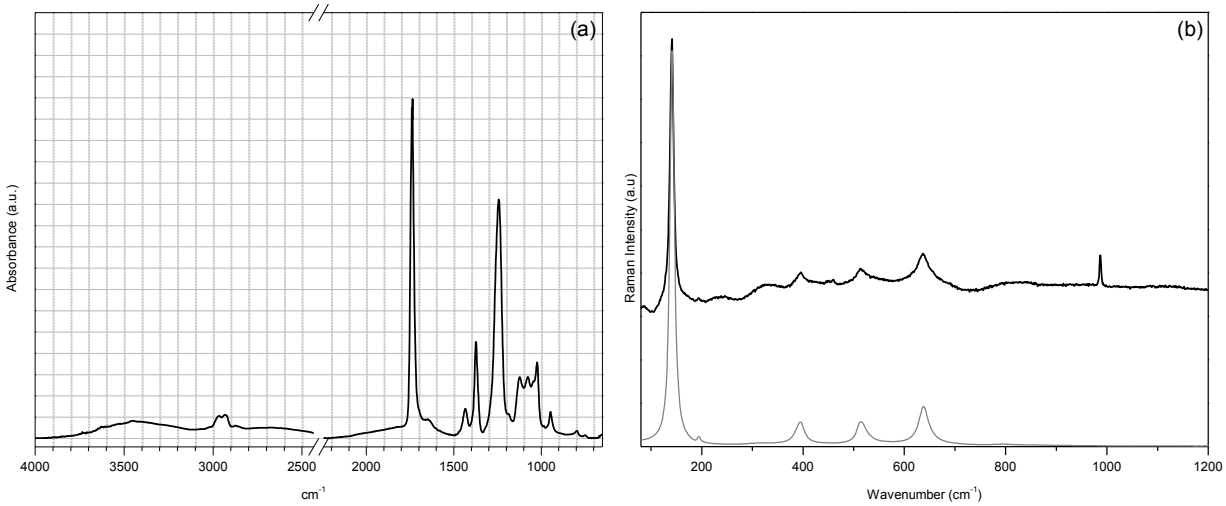


Fig. V.5. (a) FTIR spectrum of a whitish paint layer sample from *52* containing PVAc and $BaSO_4$ (b) Raman spectrum from the white anatase TiO_2 and $BaSO_4$ (—) and reference spectrum of anatase (—).

5.2 Paintings from the 90's

Paints used by Sarmento in the 90's are homemade and consist typically of dry white and black pigments mixed with an aqueous dispersion of polyvinyl(acetate) homopolymer. Uneven surfaces and textures could be found in all the paintings. Visual observation and cross-sections of samples

taken from the paintings show that some areas have enriched PVAc paint layers. Infrared spectra of paint samples taken from the *White Paintings* show similarities to artificially aged paint samples of PVAc that can be tentatively assigned to DBP release from the binder. However distribution of the binder and pigment is so uneven that liable analysis and quantification was difficult to attain.

Pintura Cega (três instrumentos de prazer e um de dor) (1990)

Curiously Sarmento painted this work (Fig. II.8) with his eyes closed (hence the name *Pintura Cega,* "Blind Painting") and with the left hand.

Fig. V.6: Detail of the white paint layer in *Pintura Cega* (canvas #1) (above) and the corresponding cross-section viewed on the optical microscope (polarized light, Obj. 10X) (below)

This painting is made from four juxtaposed canvases. Two were painted black and have very smooth and regular surfaces while the other two were painted in white with a very irregular and heterogeneous layer. Binder and pigment were mixed roughly therefore the white paint has areas that are either richer or poorer in the vinyl binding medium. Visually it seems that matt paint areas correspond to higher pigment loading that produce a diffuse light-scattering surface. Whereas glossier areas correspond to areas richer in binding medium that decrease the surface roughness of the paint.(See Fig. V.6) A thin wash of black paint can be seen unevenly poured and spread over the surface. As analyzed by FTIR this was made with a vinyl based paint.

A cross-section of the white paint shows a surface richer in the PVAc binding medium. Moreover, FTIR spectra of the upper part of the layer showns PVAc with little pigment; spectra taken from the bottom part of the paint layer shows more lithopone pigment and carbonate filler than vinyl binder.(Fig. V.7) This uneven distribution could seen in the majority of the works from this period.

This heterogeneity results either from the paint being unevenly mixed from the beginning or, because as the paint dried there might be additional agglomeration of pigments occurring during film formation and loss of water. Tiarks et al. have seen a similar effect when studying the formulation effects of waterborne acrylic binders on the distribution of TiO_2 pigment particles in paints.[115] During film formation larger titanium white clusters tend to settle down and only smaller aggregates stay at the surface.[115] The pigment

particles gather at the bottom side of the paint film due to their higher density whereas the less dense binder particles form a polymer film on top.[115]

Yellowish glossy binder is preferentially deposited in concave spaces. This yellowish discoloration seems to be intrinsic to the paint in itself in the thicker areas of paint. The thin layers of vinyl white paint remain white. Infrared spectra of the whiter and of the yellowish areas showed no significant chemical difference between the two areas. Both suffered from loss of plasticizer.

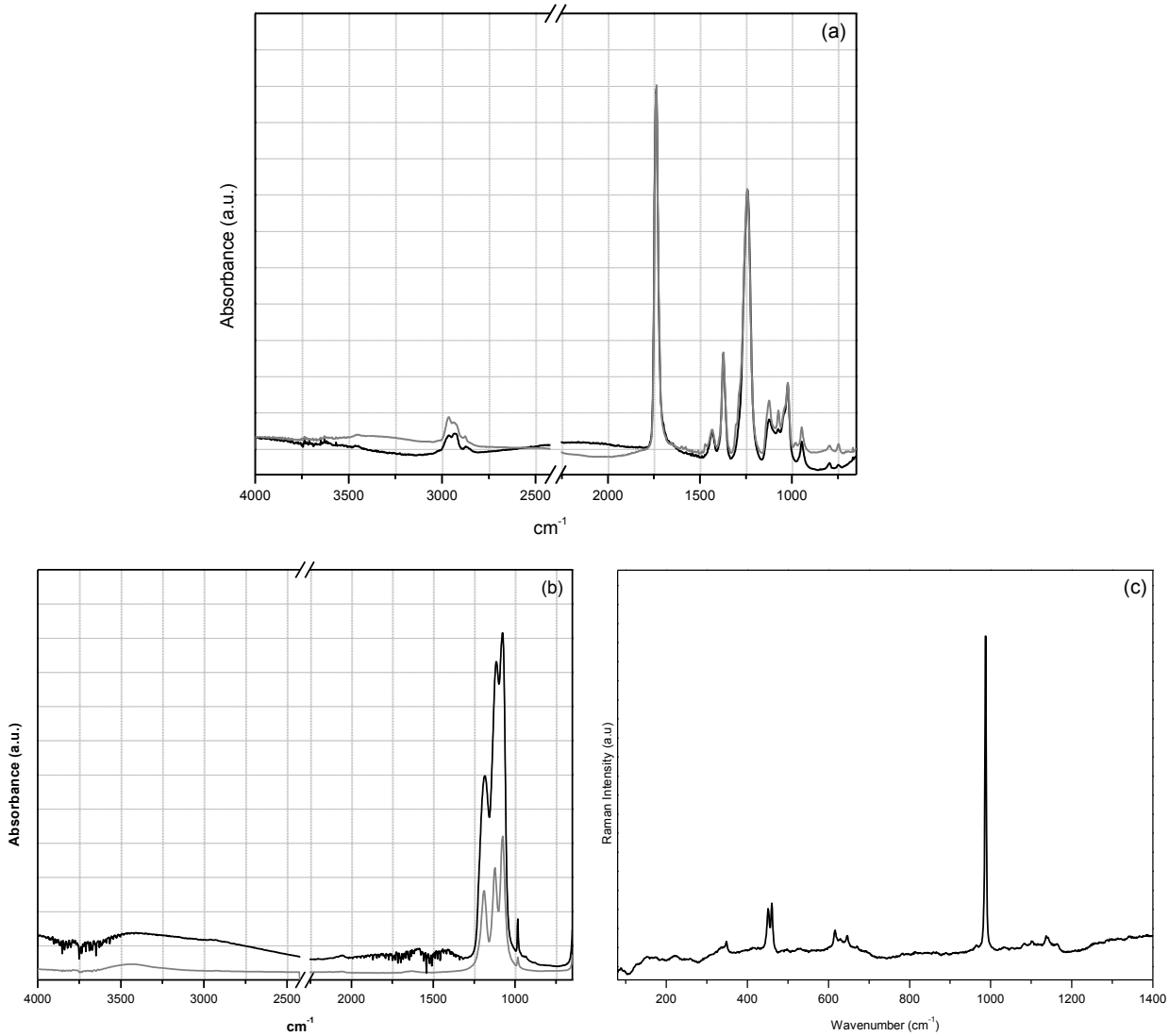


Fig. V.7: (a) Infrared spectra of the surface richer in binder of the paint sample shown in Fig. V.6 (—) and a reference spectrum of *Vulcano V7* (—) (b) Infrared spectra of the inner part of the same sample richer in pigment (—) and a reference spectrum of barium sulphate (—) (c) Raman spectrum showing the white pigment is lithopone.

***I don´t want to go to sleep* (1991)** (Fig. II.7)

The white paint's surface is similar to *Pintura Cega (Quatro instrumentos de prazer e um de dor)*: matte and whiter areas of PVAc paint stand out against glossy and white/yellowish emulsion paint. However the surface is visually more regular than the previous described work.

The painting has extensive areas of paint that have discolored and in this case yellowing seems to be more clearly restricted to thicker paint. Infrared spectra from white and discolored paint are similar. The analyzed yellowish layers show signs of additive loss as do the whiter paint

samples.(Fig. V.9) This painting has presumably suffered damage from a flood. The bottom margin seems to have been in contact with water leaving greyish and brown areas in the paint layers. These areas were sampled to assess the conservation state of the paint layers after exposure to water and no difference could be detected in the infrared spectra of untouched areas and damaged areas.

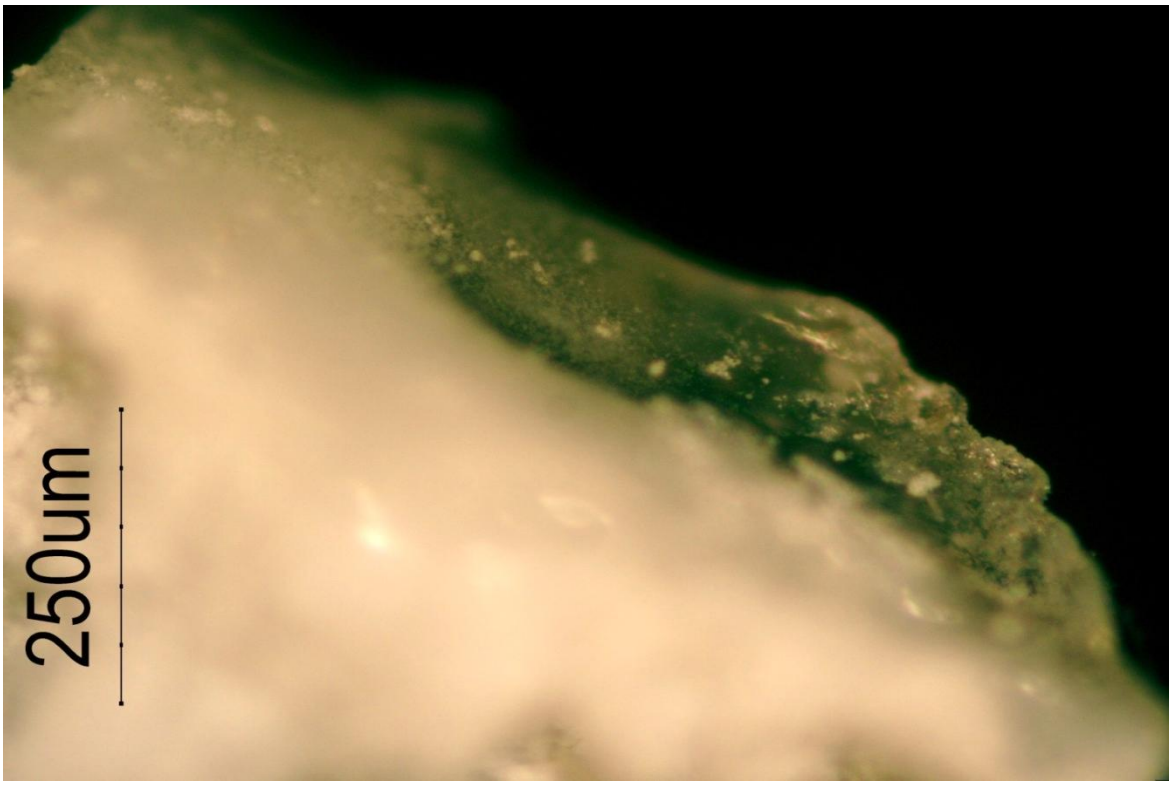


Fig. V.8: Sample from *I Don't want to go to sleep*, on the microscope (reflected polarized light, 10x) showing a yellowed, transparent top layer of almost pure binder.

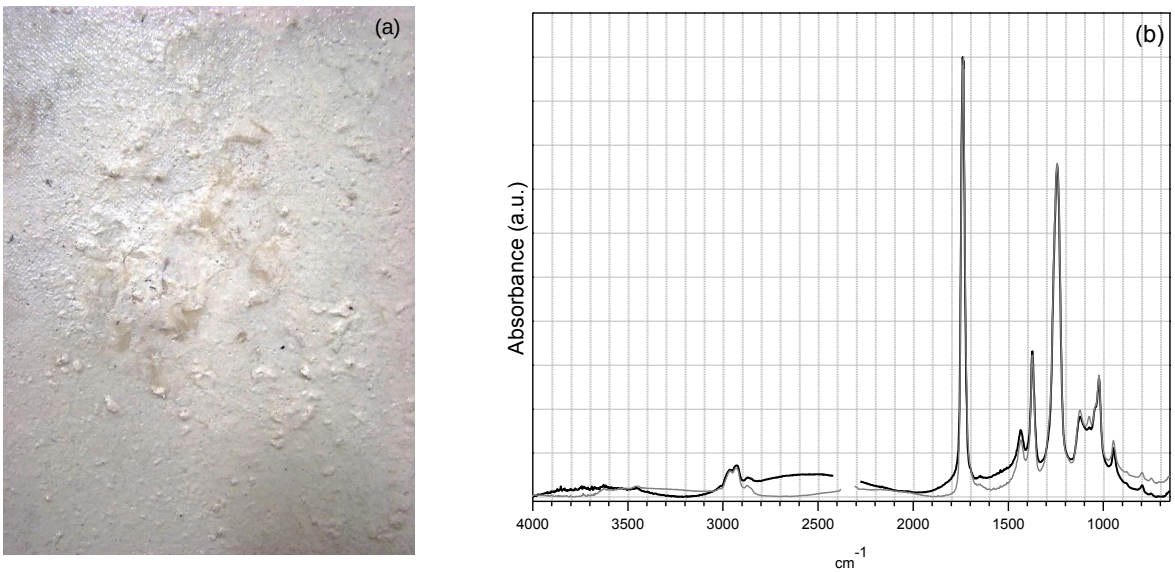


Fig.V.9: (a) Detail of the white paint layer.
(b) FTIR spectra of the PVAc binder (—) and a discolored area (—).

***Wasting my time with you* (1991)**

This work (Fig. II.9) was created with a white painted canvas juxtaposed to a black painted canvas. The white paint surface is alike the two previous works: binder and pigment are poorly mixed and irregularly distributed over the surface. Areas of thinner paint are more matte probably because the canvas has drenched out the binder.(Fig.V.10) The uneven distribution of pigment and binder in the black paint layer (Fig. V.11) and the rough surface that was created suggests that the black vinyl paint was probably handmade with white glue and black dry *Cenógrafa* pigment. The white painted canvas has extensive areas of paint that have yellowed. Discoloration seems to be more restricted to thicker areas of paint, while thinner layers seem to retain their whiteness. µ-FTIR spectra show that whiter, yellowish layers and black paint have all suffered the loss of plasticizer.

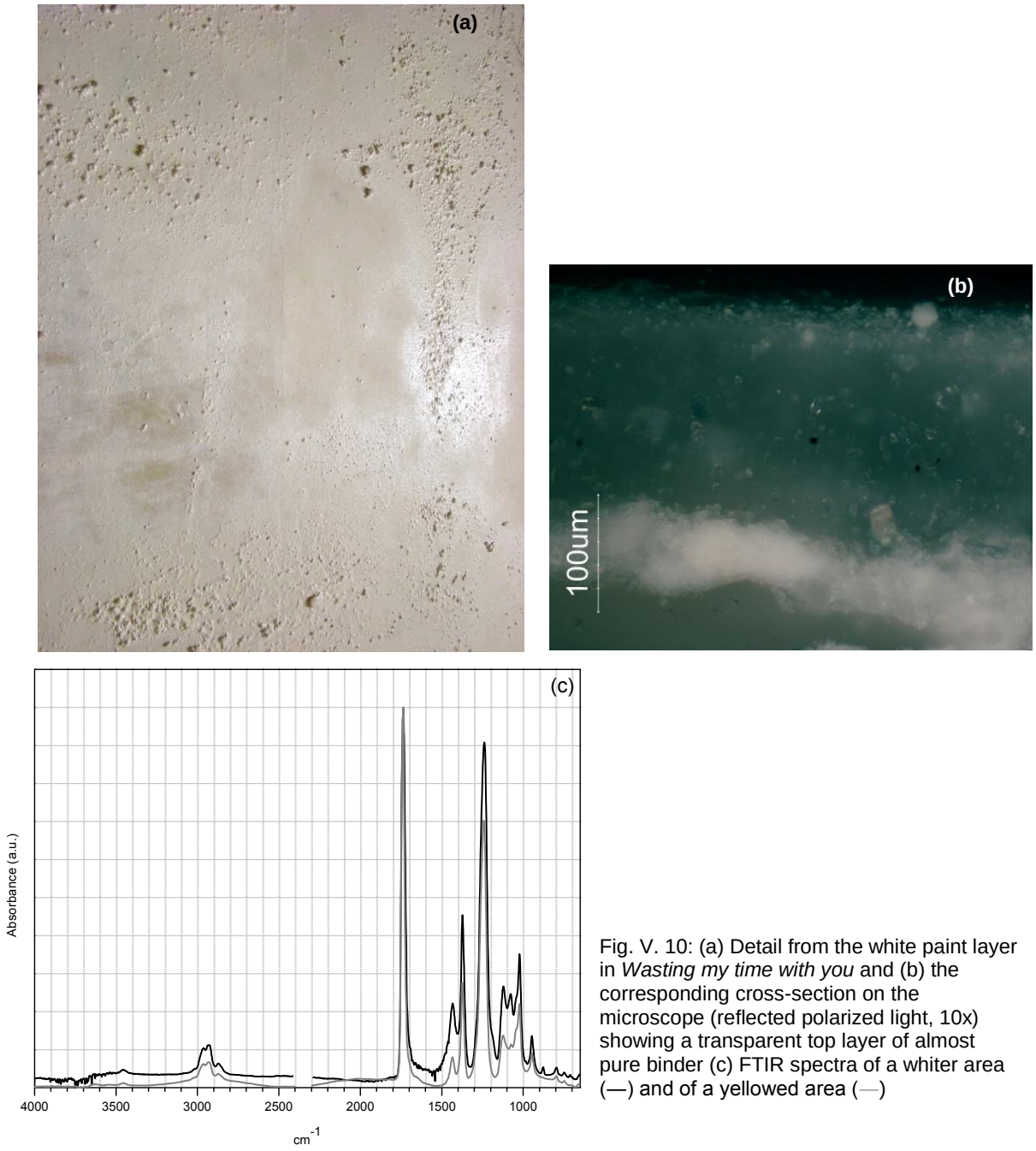


Fig. V. 10: (a) Detail from the white paint layer in *Wasting my time with you* and (b) the corresponding cross-section on the microscope (reflected polarized light, 10x) showing a transparent top layer of almost pure binder (c) FTIR spectra of a whiter area (—) and of a yellowed area (—)

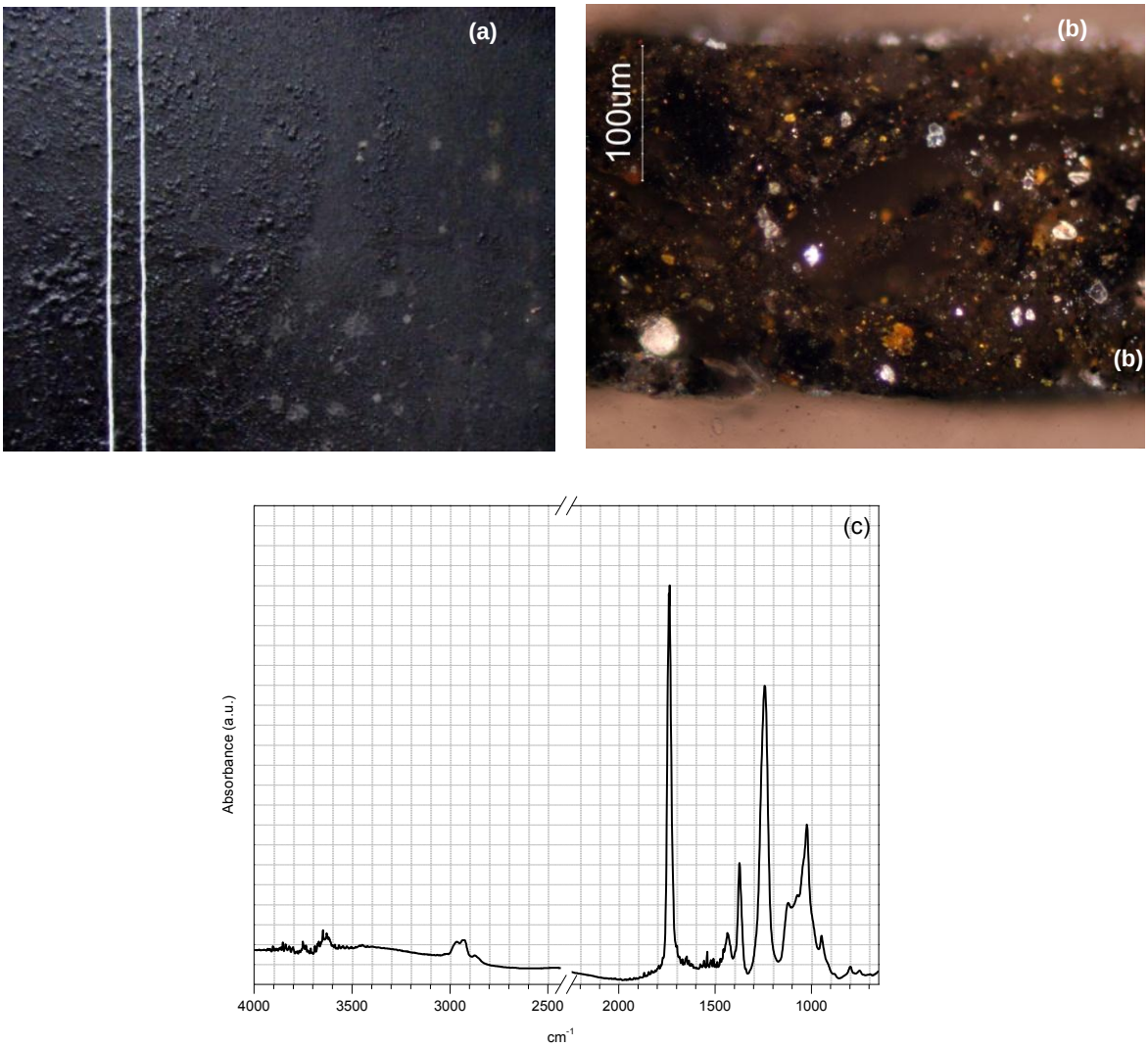


Fig. V. 11: (a) Detail from the black paint layer in *Wasting my time with you* (b) Cross-section from this paint layer (reflected polarized light, 10x) (c) FTIR spectra showing the PVAc binder and the loss of additive.

Frozen Leopard (1991-92)

A red painted canvas is juxtaposed to a white painted canvas. In both, areas rich in pigment protrude from the surface and areas of pure binder can be visually distinguished. No varnish is used to protect the surface but the graphite drawing was locally protected with a fixative. In the earlier years Julião would apply a cheaper hairspray. But the paintings would retain a hairdresser smell so that was replaced with an artist's fixative from *Talens* or, *Winsor & Newton*. The fixative can be delimited with UV light (Fig. V.12) and was identified as an acrylic by µ-FTIR by the shape of the absorption bands at 2956, 2930 and 2973cm^{-1}, the carbonile stretching at 1732 cm^{-1} and the C-O/C-C stretch at 1172 cm^{-1}. (Fig. V.14).

The vinyl emulsion paint underneath this fixative shows wrinkling probably because with was not allowed to dry completely before the application of the acrylic fixative. In the white canvas in terms of discoloration the general impression is that the entire surface has a white/yellowish tone. Infrared spectra showed loss of additive in all analyzed paint samples.

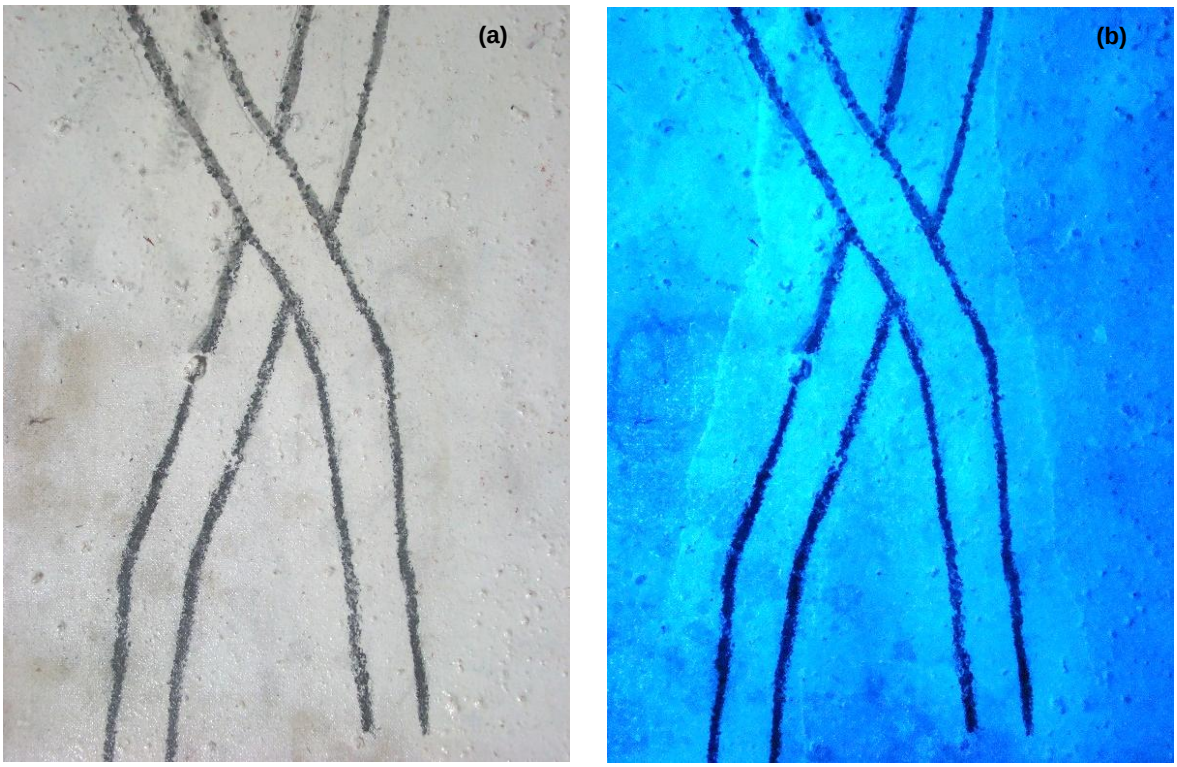


Fig. V.12: (a) Detail of the black drawing in canvas #2 of *Frozen Leopard*. (b) The same image seen under UV light shows the presence of the fixative (lighter blue colour around the drawing) applied over the graphite drawing.

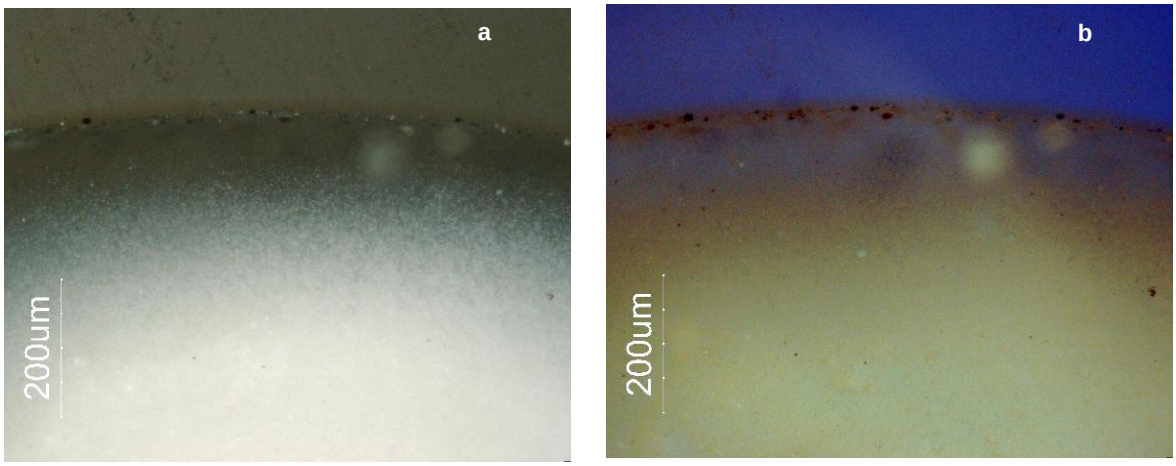


Fig. V. 13 (a) Cross section of a paint sample taken from the white background showing the upper surface richer in transparent binding medium. (b) the same cross-section see in UV light (both images taken with 20x obj.)

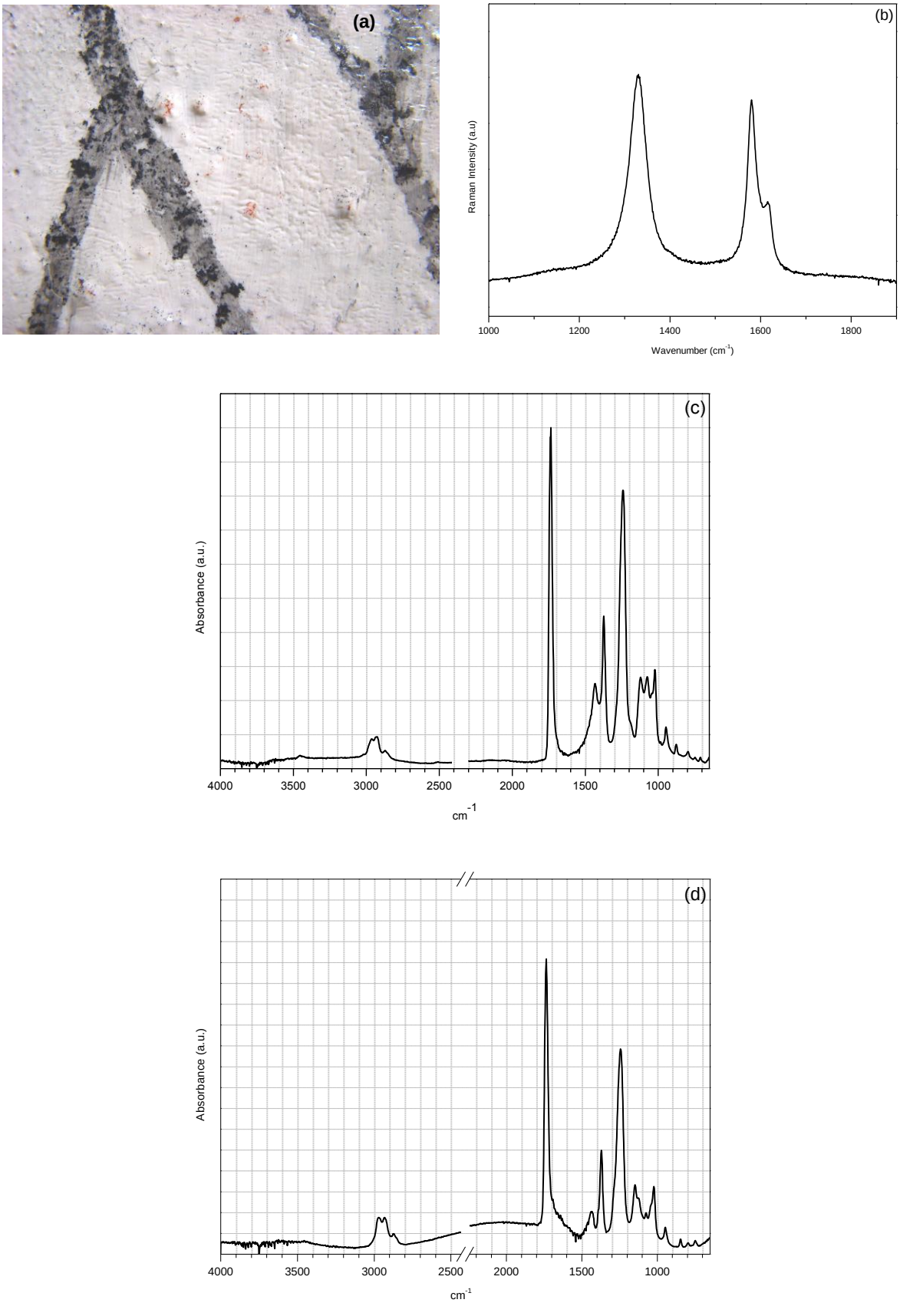


Fig.: V.14: (a) Detail of the black drawing in canvas #2. (b) Raman spectrum of the graphite (c) FTIR spectra of the PVAc binding medium (d) and of the acrylic fixative (it was not possible to separate completely the fixative coating from the paint layer).

Belém (1992)[29]

Except for *An Involved Story* (1998) (see below) *Belém*'s paint surface is smother than the other paintings from this decade. Although some pigment agglomerates protrude from the surface Sarmento mixed more thoroughly the vinyl emulsion with the dry white pigment.(Fig. V.15) This work has suffered a severe discoloration in extensive areas of paint. All the samples analyzed with infrared spectroscopy show loss of DBP plasticizer. Moreover the Py-GC/MS analysis shows that in yellowed areas there is loss of phthalic acid which (as was described in the artificial ageing studies) is most probably related to the phthalate and therefore with its disappearance from the paint.(See Fig. V.16-V.17) More yellowed paint and white paint samples would have to be analyzed in order to ascertain if it can be somewhat correlated with paint's discoloration.

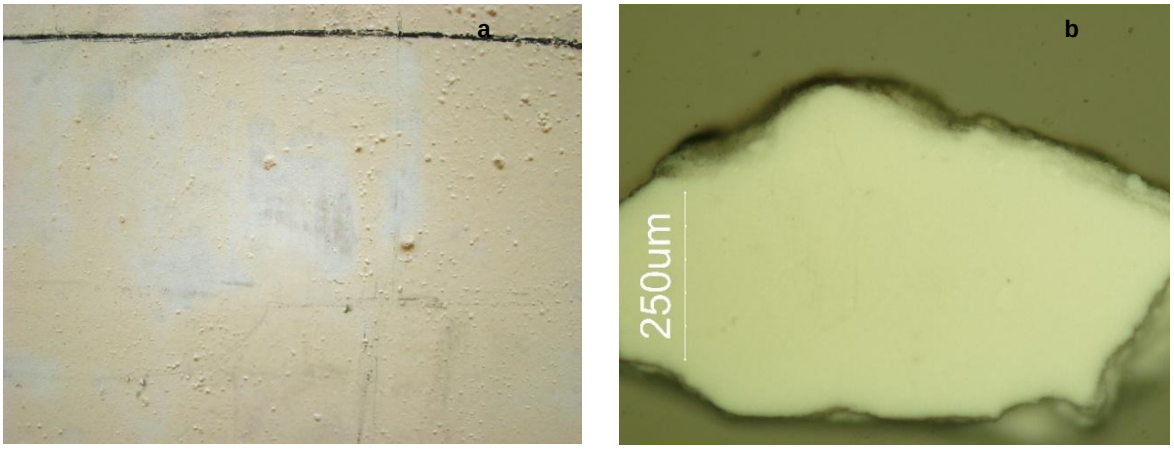


Fig. V.15: (a) Detail of the white paint layer. (b) Cross-section of the white paint showing the pigment is well distributed across the paint (reflected light, obj.10x)

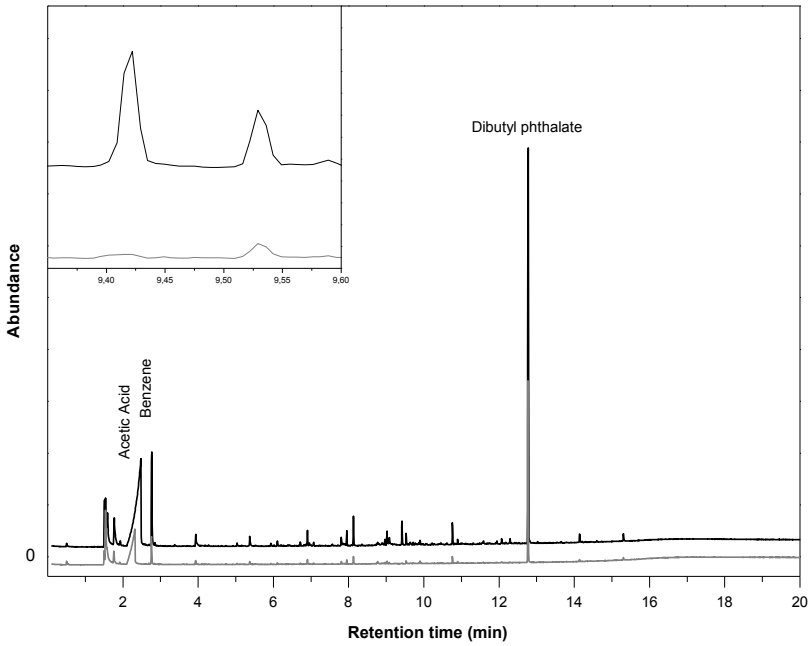


Fig. V.16: White paint pyrogram showing the PVAc homopolymer from a sample taken from a whiter area (—) and from a sample taken from a more yellowed area (—) Inlay spectrum from 9:30 to 9:60min shows the loss of phthalatic acid in the yellowed paint.

[29] The dimensions of this painting and its location make it impossible to present a good image of the painting. The artist was contacted to know if a better quality photography existed to which he explained that because of the same reasons he could not provide us with a better image.

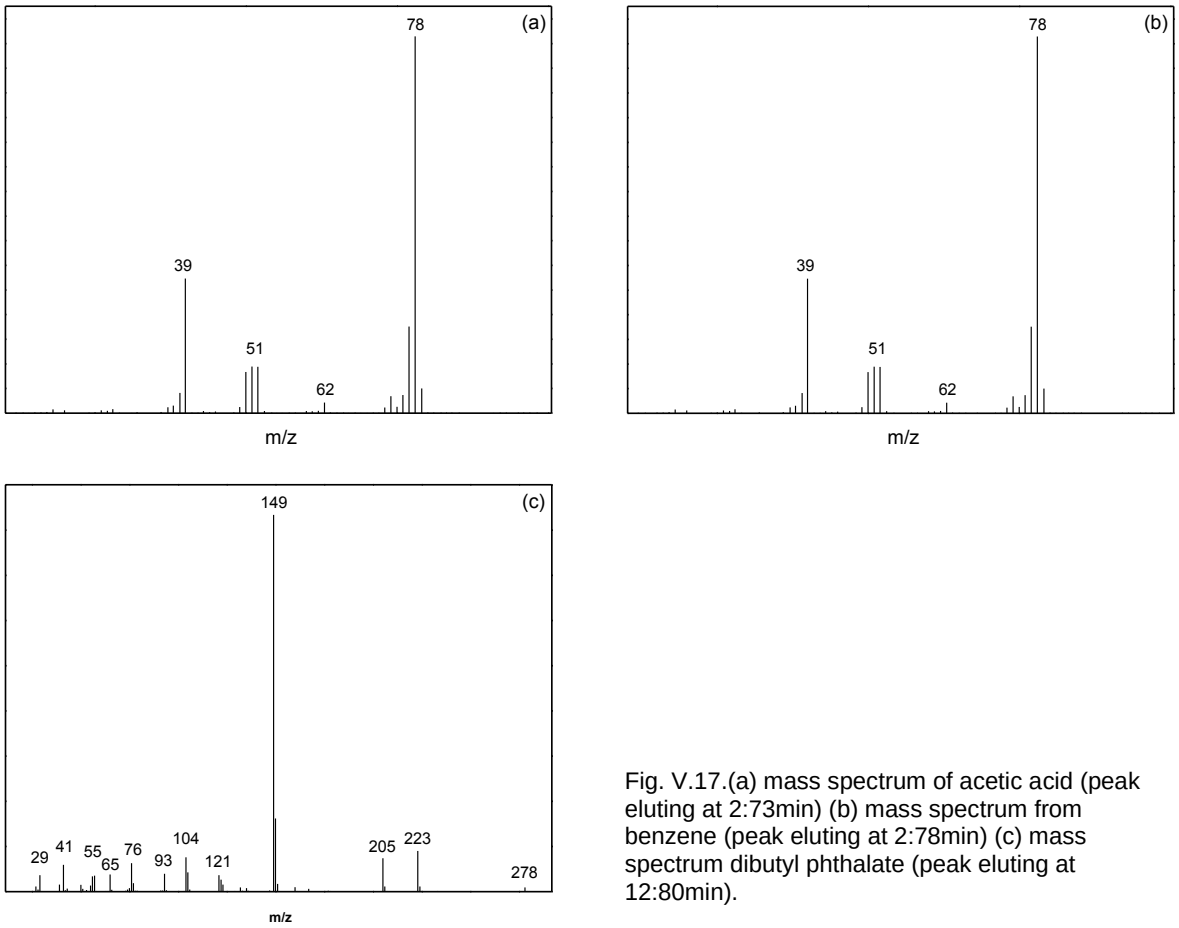


Fig. V.17.(a) mass spectrum of acetic acid (peak eluting at 2:73min) (b) mass spectrum from benzene (peak eluting at 2:78min) (c) mass spectrum dibutyl phthalate (peak eluting at 12:80min).

***An Involved Story* (1998)**

This work (Fig. II.12) has the smother surface from this studied group of paintings because Sarmento mixed very well the vinyl binder with the white pigment. Water seems to have been spilled over the wet paint leaving craters on the surface. Like *Belém* this work has extensive areas of paint that have severely yellowed. The yellowing does not seem to depend on thickness and also appears in the back of the painting where paint is protected from light. The infrared spectra only shows that phthalate was lost in the yellowed areas (Figs. V.18 and V.19).

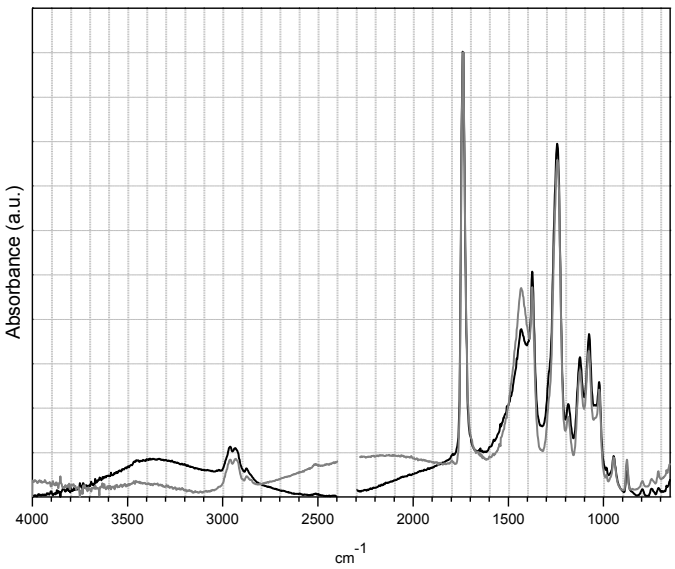


Fig.V.18: FTIR spectra of the PVAc binding medium from a white area (—) and a discolored area (—) in the white paint layer

Fig. V.19: Detail of *An Involved Story* showing the craters left by spilling of water over the surface while the paint is still wet and the differences in yellowing according to the paint's thickness.

5.3 Paintings from the XXI century

Inadequate Readings (2004)

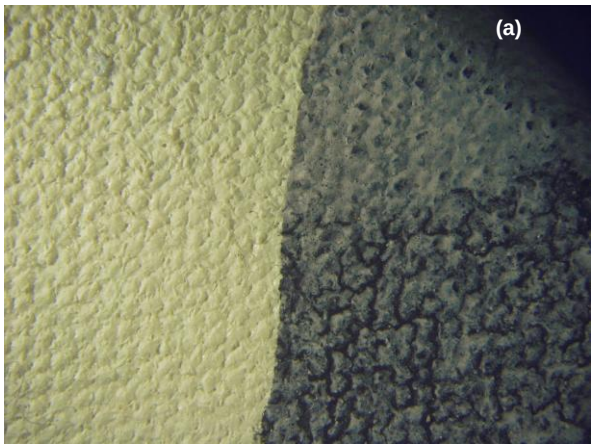


Fig. V.20: Detail of Inadequate Readings under the stereomicroscope (obj.7x) showing the white thin paint layer that covers the black painted figure.

This painting (Fig. II.4) was created with a different painting technique than the previous paintings. The white paint used in the background is still made of PVAc white glue and *Cenógrafa*. However the paint is thoroughly mixed, the surface is much more regular and the canvas weave texture shows through the paint layers. (Fig. V.20) The infrared spectrum of the black silhouette is very similar to the FTIR spectrum of modern black *Sabu* paint e.g. a PVAc terpolymer binding medium seems to be present. (Fig. V.21)

After stretching the canvas a liquid thin white layer was spread across the surface. Compared to the other paintings there is no sign of discoloration of the white paint.

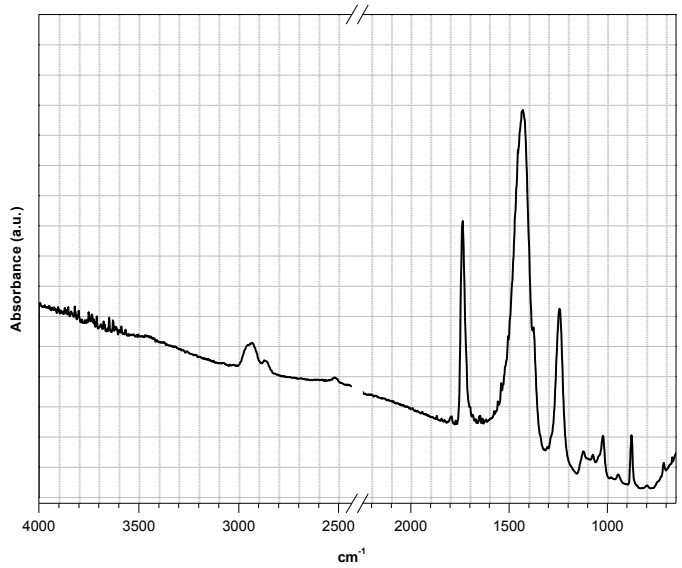


Fig.V.21: FTIR spectrum of the PVAc binding medium from the black paint a P(VAc-E-VC) terpolymer.

Inadequate Readings suffered local damage during transportation when returned from an exhibition. Due to the typical low T_g of synthetic emulsions the paint surface is tacky at room temperature and a piece of glass got accidently stuck on the paint. (Fig. V.22) After successfully removing the glass it was found that the surface's texture had been destroyed during the damage. Using the thermoplastic characteristics of the synthetic paints reconstitution of the texture was also successfully achieved.(for a complete description see Appendix VI: Treatment of *Inadequate Readings*)

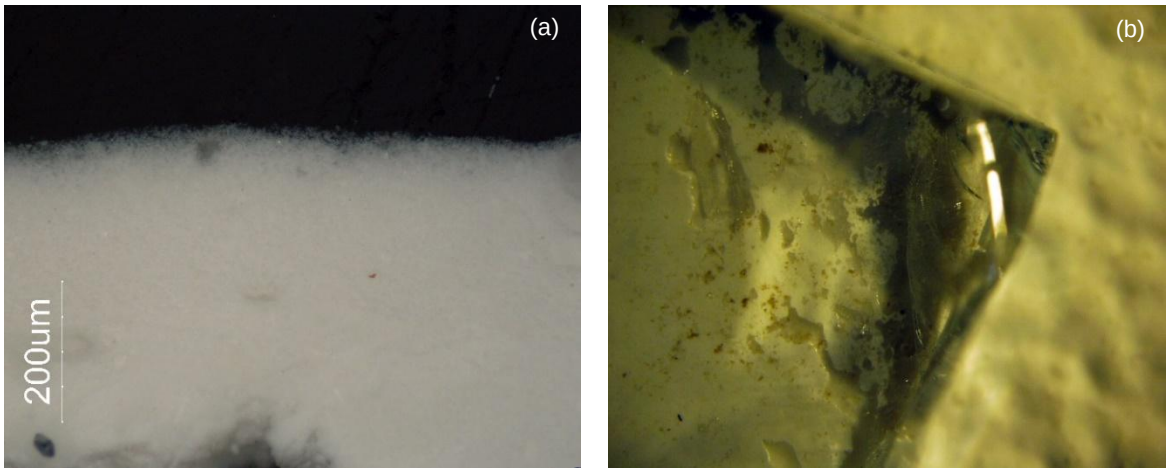


Fig. V. 22: (a) Cross section of a paint sample taken from the white background showing that the pigment is more evenly distributed over the surface (10x obj.) (b) Detail showing how the paint was smashed under the glass. (Obj.20X)

Heldér (2008) (Fig.II.15)

Cross-sections from *Helder* and infrared analyzes show that in this work a thin white coating of acrylic gypsum was applied over a vinyl and TiO_2 rutile underlying paint layer. The x-section under polarized light shows what it seems to be a unique white paint layer. However, when UV radiation is used three distinct layers are seen.(Figs. 23 and V.24) FTIR and Py-GC/MS analyzes conduted on this upermost paint layer revealed an acrylic binder, a poly(ethylacrylate-methyl methacrylate), in the inner paint layers the presence of a PVAc binder was revealed.(Fig. V.25 – V.27) Furthermore in *Hélder* layers of two shades of gray and yellow acrylic paint were used to create

the painted motif. The painting's surface is irregular. In some areas the paint forms a shiny surface in others the texture is a result of the canvas threads and of tiny agglomerates of badly dispersed pigment. No signs of discoloration were found in this work.

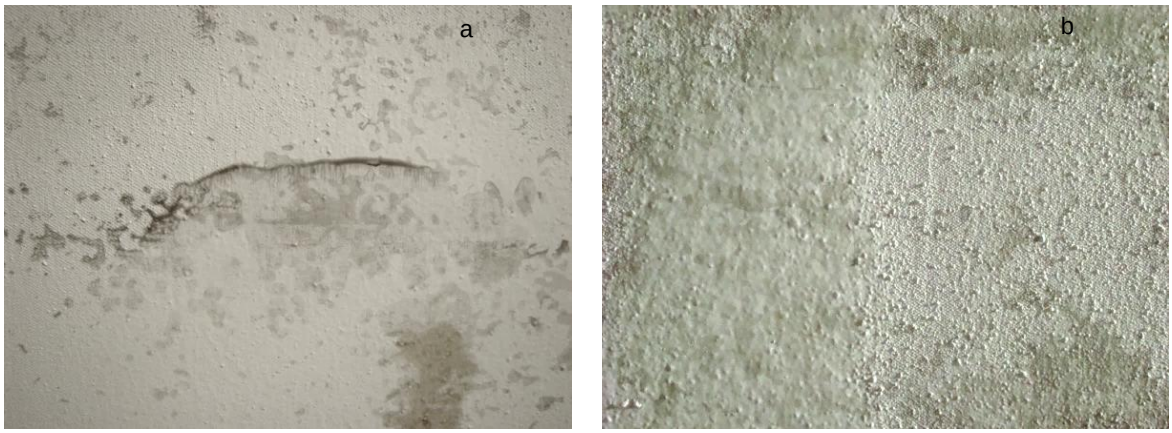


Fig. V.23: (a) Detail of *Helder* with the two white and grey and yellow paint layers. (b) Detail under ranking light accentuating the differences in surface texture.

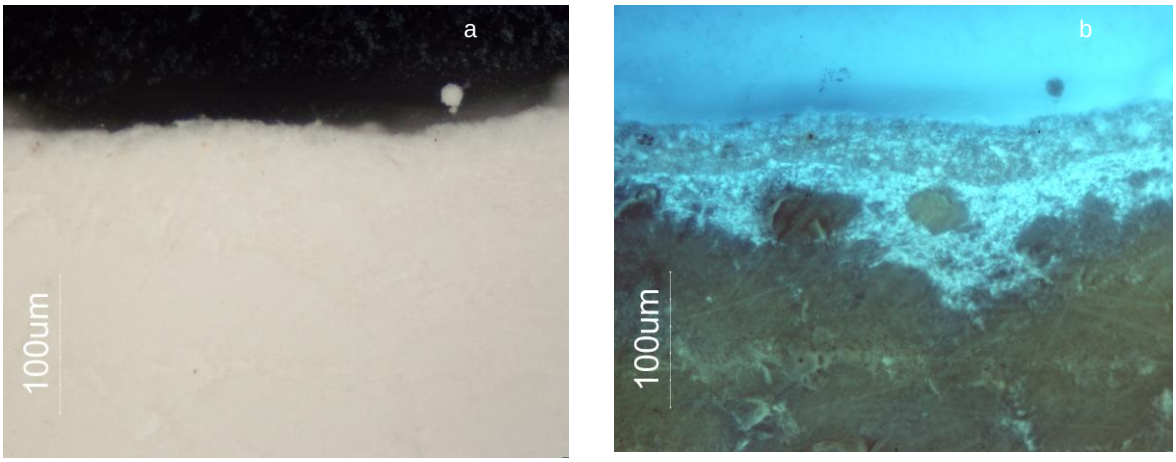


Fig. V.24: (a) Cross-section under polarized light (b) and under UV blue. (Obj 20x).

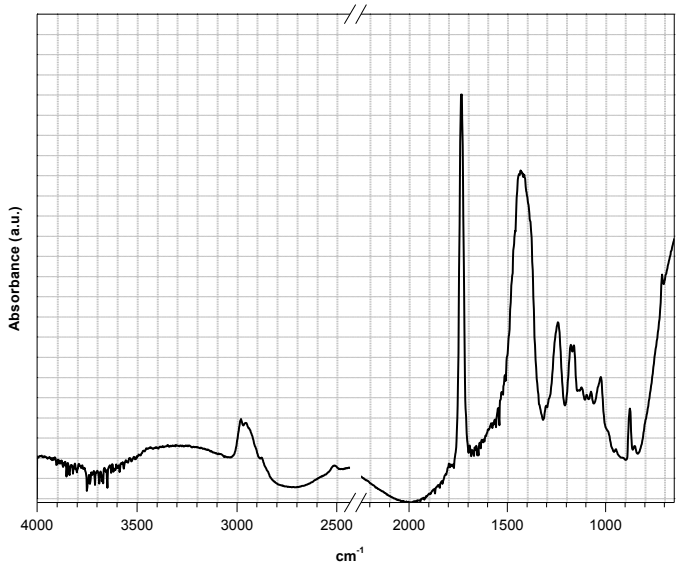


Fig. V.25: (a) FTIR spectrum of the upper paint layer done with p(EA-MMA)

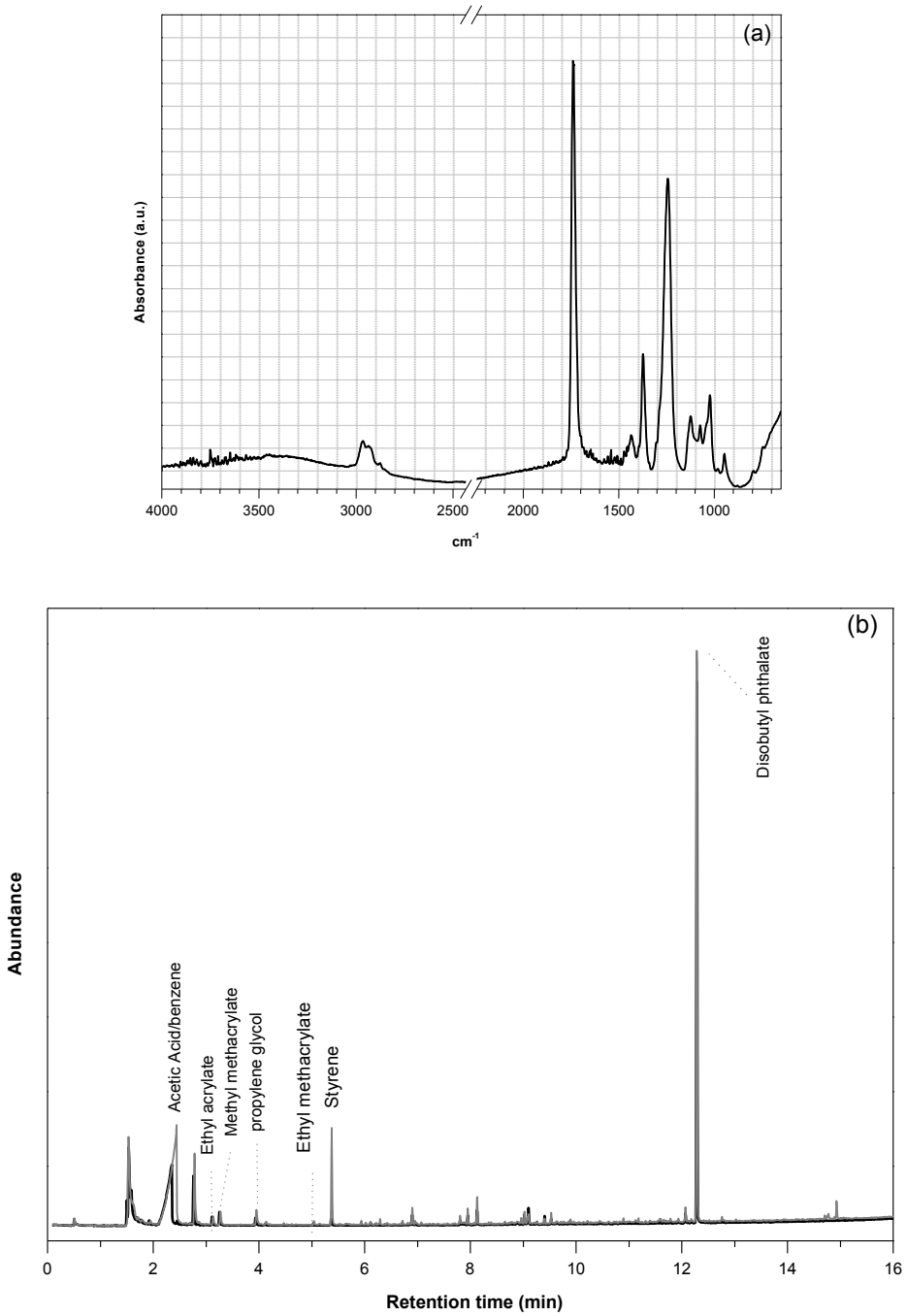


Fig. V.26: (a) FTIR spectrum of the underlying paint layer created with PVAc (b) Pyrogram showing the acrylic binder on the satin white (—) and vinyl binder on the matte white paint (—).

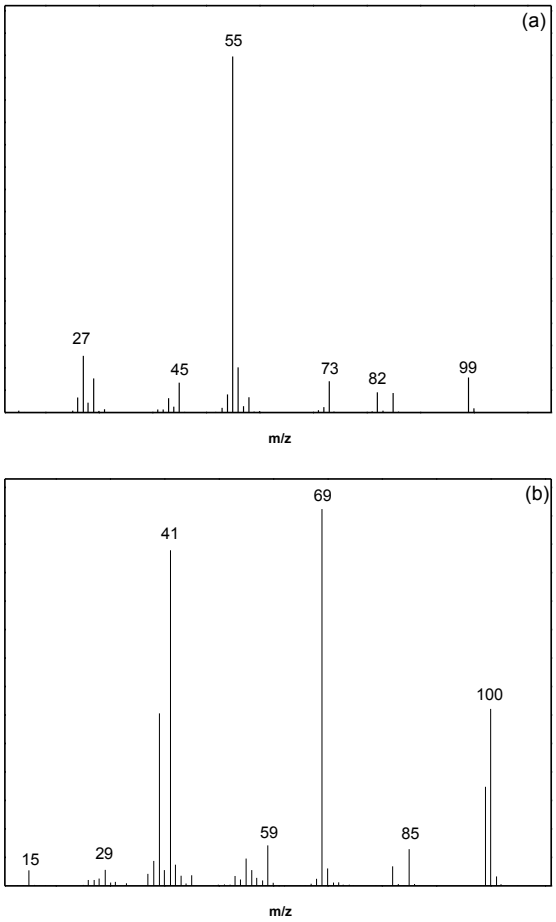


Fig. V.26: (a) mass spectrum of ethyl acrylate (peak eluting at 3:14min) (b) mass spectrum from methyl methacrylate (peak eluting at 3:28min)

5.4 Loss of additive from the paint layers

The FTIR spectra from almost all the samples analyzed showed loss of additive which is visible mainly in the CH group stretching as the band at 2964cm^{-1} loses intensity when compared to the band at 2926cm^{-1}. Exceptions are the painting *An Involved Story* were the samples corresponding to the whiter areas still show the presence of plasticizer in the FTIR spectra. Also in *I Don't want to go to sleep* the plasticizer can still be found in more internal areas of the analyzed samples. Importantly, in *Frozen Leopard* the PVAc binder seems to have remained protected under the layer of acrylic fixative. Unfortunately most bands due to the dibutyl phthalate plasticizer (identified in two of the case studies, *Belém* painted in 1992 and *An Involved Story* from 1998) are masked by the $CaCO_3$ and $BaSO_4$ absorbance. Therefore the disappearance of the additive could only be quantified by FTIR using the C–H stretching region. Although quantitative analysis of absorbance ratios were carried out, all differences encountered are within experimental error and therefore no comparative conclusions can be drawn. Furthermore, no significant differences were found in the carbonile stretching absorptions. (See Table V.1 and Appendix IV)

Table V.1: Values of peak centre (μ), area (A) and full width at half maximum (σ) calculated by fitting the νC=O absorption with a Gaussian function The values are the average of three infrared spectra taken from each sample. Spectra were baseline corrected and normalized by the intensity of the C=O absorption band.

Paintings	Colour	μ	A	σ
52	Black	1738	22.41 ± 0.37	22.91 ± 0.35
	Red	1736	19.94 ± 0.59	25.41 ± 0.59
	Yellow	1738	21.22 ± 0.84	22.70 ± 0.56
	White	1739	18.83 ± 2.05	22.86 ± 0.53
	White/yellowish	1738	21.59 ± 1.13	22.87 ± 1.12
Salto	Black	1738	21.74 ± 0.77	23.10 ± 1.07
	White	1738	22.12 ± 1.77	23.93 ± 1.60
	Blue	1735	21.19 ± 0.08	32.01 ± 2.82
	Red	1739	21.20 ± 1.52	22.72 ± 0.36
White background	White paint	1737	23.84 ± 1.87	24.31 ± 1.67
	Yellowed paint	*1737*	*22.34 ± 0.84*	*23.40 ± 0.50*
I don´t want…	White paint	1738	21.83 ± 1.38	22.56 ± 0.92
	Yellowed paint	*1737*	*23.19 ± 1.42*	*25.53 ± 1.94*
Wasting my time	White paint	1738	23.51 ± 1.06	23.88 ± 0.79
	Yellowed paint	*1737*	*23.95 ± 2.61*	*24.62 ± 2.25*
	Black paint	1738	23.79 ± 3.81	24.40 ± 3.11
Belém	White paint	1738	22.89 ± 1.35	24.01 ± 0.63
	Yellowed paint	*1737*	*24.26 ± 0.93*	*24.57 ± 0.52*
Pintura Cega…	White paint	1737	22.16 ± 1.36	22.83 ± 0.98
	Yellowed paint	*1738*	*23.00 ± 0.64*	*23.64 ± 0.39*
	Black paint	1738	22.81 ± 1.19	23.24 ± 0.77
Frozen Leopard	White paint	1737	23.34 ± 1.01	23.81 ± 0.67
	Yellowed paint	*1738*	*22.74 ± 1.33*	*23.22 ± 1.00*
	Red paint	1737	23.55 ± 0.96	23.82 ± 0.73
An Involved Story	White paint	1737	23.02 ± 1.26	24.44 ± 0.57
	Yellowed paint	*1738*	*23.83 ± 1.44*	*24.71 ± 0.70*
Inadequate Readings	White paint	1737	23.48 ± 1.31	24.22 ± 0.97
	Black paint	1736	22.37 ± 1.23	23.93 ± 0.71
Helder	White paint	1738	22.07 ± 0.63	23.43 ± 0.55

5.5. Paint discoloration

Discoloration of the white paint is a major concern for works painted in the 90's. The degree of yellowing was measured by colourimetry (Fig. V.27 and Table V.2) so that compative data could be obtained. The degree of yellowing does not seem to be correlated with the aging time of these paintings, however it can apparently be correlated with differences in the way the artist works his paints (e.g. more pigment and/or filler, binder's distribution and layer thickness).

Paintings were the binder and pigment are thoroughly mixed and have regular surfaces like *Belém* and *An Involved Story* present higher values of b*, 13.68 ± 3.63 and 17.79 ± 2.24 respectively. Paintings where both binder and pigment were randomly mixed and the texture is more irregular primarily show yellow areas where there is more binder: *Pintura Cega (três intrumentos de prazer e um de dor)*, *I Don't want to go to Sleep* and *Wasting my time with you* have b* values of 11.27 ± 1.76 and 10.72 ± 0.34 for the two white canvas of *Pintura Cega*; 11.88 ± 1.61 and 11.08 ± 0.71 for the other two paintings respectively. *Frozen Leopard* (1991/92) also has an irregular texture however paint thickness seems to be more even over the all surface (suggesting that the paint is more evenly spread over the support) and shows lower values of b* 8,03 ± 1.41.

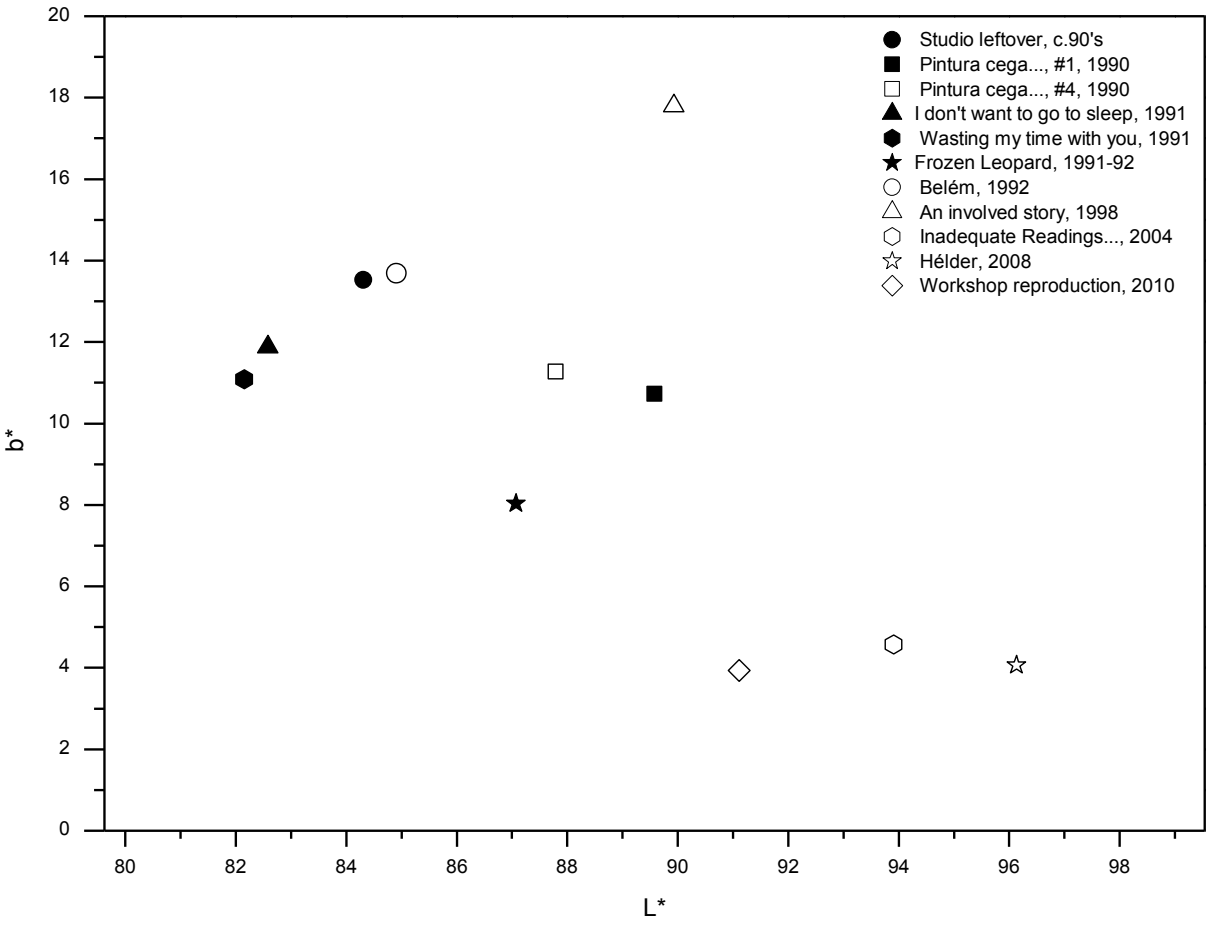


Fig. V.27: Representation of the L* and b* values of the studied *White Paintings*.

Table V.2: L*, a*, b* values of whiter and yellowed areas of the paintings studied.

	Whither areas			Yellow areas		
	L*	a*	b*	L*	a*	b*
Pintura Cega, Canvas # 1, 1990	86,99 ±0,95	0,39 ±0,12	5,28 ±0,52	89,58 ±0,13	0,42 ±0,16	10,72 ±0,34
Pintura Cega, Canvas # 4, 1990	88,80 ±1,28	-0,06 ±0,14	5,20 ±0,33	87,79 ±0,98	-0,37 ±0,33	11,27 ±1,76
I Don´t want to go to sleep, 1991	—	—	—	82,58 ±3,25	1,08 ±0,54	11,88 ±1,59
Wasting my time with you, 1991	—	—	—	83,29 ±1,61	0,64 ±0,01	10,80 ±0,40
Frozen Leopard, 1991-92	87,35 ±2,12	-0,12 ±0,72	6,20 ±0,07	87,07 ±2,69	-0,12 ±0,48	8,03 ±1,41
Belém, 1992	87,01 ±0,62	-0,30 ±0,29	8,05 ±0,56	84,91 ±1,29	0,39 ±0,45	13,68 ±3,63
An Involved Story, 1998	89,46 ±5,14	-0,11 ±0,35	6,11 ±0,08	89,93 ±0,84	0,07 ±0,57	17,79 ±2,24
Inadequate readings, 2004	93,91 ±0,64	-0,25 ±0,08	4,57 ±0,36	—	—	—
Hélder, 2008	96,13 ±0,16	-0,51 ±0,04	4,06 ±0,09	—	—	—

Discoloration seems to be a superficial effect. (Fig. V.28) In cases where the paintings suffer damage the paint underneath remains white. This effect is easily explained if photochemical reactions are taken into account as it is usually a surface phenomena that depends on the degree of light penetration into the layer. Also, if oxygen is involved the diffusion rate of O_2 through the paint layer explains why discoloration is limited to the outer surface. Moreover, if yellowing is a result of polyene structures, these strongly absorb incident radiation, and these may be acting as a protective layer preventing photodegradation of internal zones of the paint. [92]

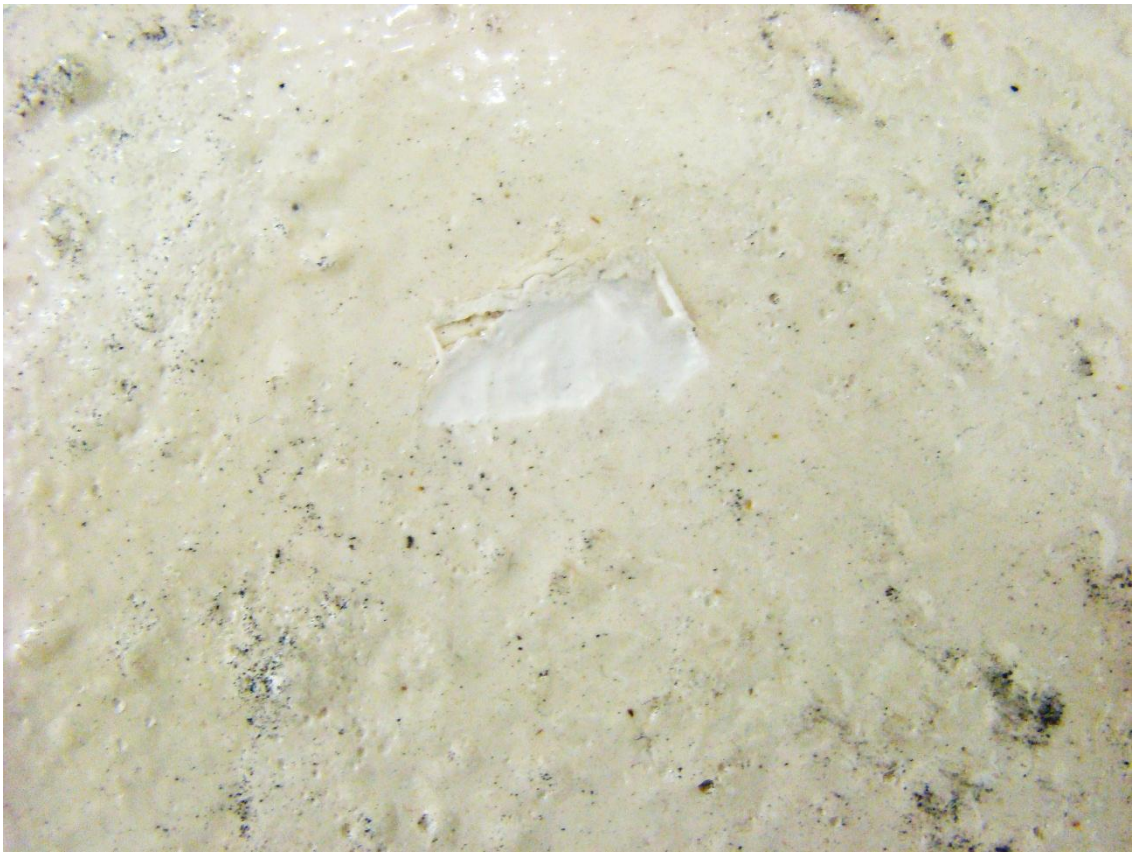


Fig. V.28: Detail of I don´t want to go to Sleep painted in 1991. Damage of the surface left part of the inner layer visible. The paint remains white inside while the surface has yellowed.

5.6. Conclusions

All the paintings studied can be correlated with the choice of materials and methods described in chapter II.

The two paintings from the 80's (*Salto and 52*) demonstrate Sarmento's choice for a wide-range of textural effects and a more varied palette. It is interesting to note that some of the paints analyzed contain a PVAc-VeoVa copolymer which can be correlated with the identified formulation on the old *Sabu* jars found in the artist's studio. Even the presence of the filler (kaolin) is commom to both case studies and the paint jars.

The analyzed paintings from the 90's the designated *White Paintings* serie were painted with a PVAc homopolymer based emulsion, most probably the *Vulcano V7*. However an important difference can be found in correlation with the glues analyzed and the paintings studied. DiBP was found on the emulsion Vulcano *V7* but, DBP was found in the case studies. Moreover this set illustrates Sarmento's exploration of the binder/pigment ratio in his homemade paints. From an irregularly mixed paint with an uneven distribution over the cotton canvas (*I don´t want to go to sleep*, *Wasting my time with you, Pintura Cega* and *Frozen Leopard*); to a thorough mixture

between binder and pigment that was more evenly spread over the textile support (*Belém* and *An Involved Story*).

Inadequate Readings from 2004 still follows the trend of using a PVAc white glue with *Cenógrafa* white for the white background however it would be important to identify the phthalate used in the emulsion. *Vulcano V7* bought in that year and analyzed for characterization purposes already contains DiBP therefore there is a possibility that in this painting DiBP might be present. Interestingly the black paint layer shows that the terpolymer is present. That suggests that Sarmento used the 'modern' *Sabu* black paint and not a homemade paint.

Finally *Helder* illustrates Sarmento's choice to change his materials and painting methods to avoid the yellowing observed in the paintings from the 90's. The pigment used is now rutile titanium dioxide and a thin layer of acrylic and TiO_2 rutile covers the surface.

In accordance with what was observed during artificial aging infrared spectra shows that the only chemical change that is taking place is the loss of phthalate from the paint. Py-GC/MS analyzes conducted on two of the paintings that showed a more severe case of yellowing (*Belém* and *An Involved Story*) do not show signs of the phthalate being degraded. That suggests that the degradation of this additive might only be related to the DiBP but, does not happen to DBP. Therefore, yellowing is presumably not directly related to the photodegradation of the phthalate.

An important conclusion could be drawn when comparing the b* values of the yellowed paintings in relation to their creation date. *Belém* painted in 1992 and *An Involved Story* painted in 1998 are much more yellow than paintings created in 1990 or 1991 (for instance *Pintura Cega* and *Wasting my Time with you*, respectively). The main difference found in these paintings is that binder and pigment are homogeneously mixed and distributed in the more yellowed paintings.

Artificially aged samples of *V7 + Cenógrafa* white showed negligible yellowing of the paint samples specially when compared to the high b* values measured in the case studies (naturally aged between 24 to 16 years) several reasons can be proposed: different phthalate component , the pigment/binder ratio is diferent (the binder ratio used by Sarmento is much higher than the one used in the laboratory reproductions; the thickness of the paint layers in the paintings is considerably higher than the one used to create the reproductions; the irregularity in the binder/pigment dispersion is much higher in the case studies; the use of a cotton canvas as a 'substrate'; (and the lighting conditions as paintings exposed in Museums or galleries are usually exposed to light/dark cycles according to their opening schedule).

Hélder painted 6 years ago does not show signs of yellowing and presents a very low b*value and no loss of additive from the PVAc paint layer. That is in agreement with the results obtained for artificial aging where rutile white pigment showed to have a high stabilizing effect on the binder.

VI. Natural aging: discoloration of Sarmento's paints

In order to better understand the yellowing occurring in the paintings described in the previous chapter a new set of samples was prepared. In an attempt to pinpoint the factor (or factors) behind the discoloration observed in the case studies this new set addressed characteristics of the paintings that were not present in the samples used in the artificial aging tests.

These characteristics were: emulsion formulation (phthalate content); pigment nature; support, paint thickness; and, exposure conditions in a natural environment with exhibition in illumination cycles or, dark exposure when the paintings are stored. A schematic of the set can be seen in fig. VI.1. Besides these prepared samples a mock-up prepared by Sarmento himself was used to study the influence of light and dark exposure conditions on the degree and reversibility of the yellowing.

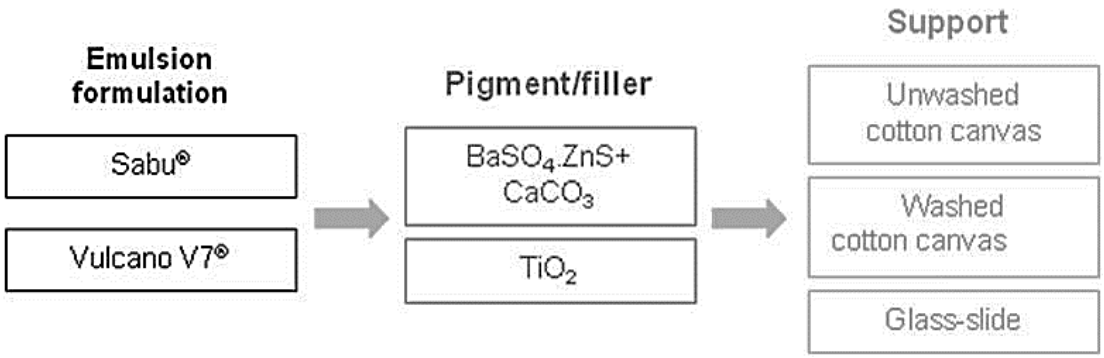


Fig. VI.1: Schematic of the samples prepared and studied in natural aging

The binder pigment proportions used were different from the ones used for artificial aging. All the paints were prepared following Sarmento's indications with a ratio binder/pigment of 70%/30% (w/w) that is more binder was used in this set than in the artificial aging experiment. A small quantity of water was added to achieve the "creamy" consistency recommended by the artist in order to obtain a workable paint. Following the artist methodology, whenever canvases were used as a support these were wetted immediately before paint application. The paint was applied using a film applicator and superimposed glass-slides so that thicker layers (the wet film was 1,2mm thick) alike the ones found in the case-studies could be achieved. Reproducing Sarmento's choices of materials and techniques, a set of the vinyl emulsions plus *Cenógrafa* white where coated with a very thin layer of diluted acrylic gypsum from *Talens*. All samples (applied in glass slides or canvas) were the size of half a glass slide large and two duplicates were used for each paint (Fig. VI.2).

The following exposure conditions were used for the samples kept in the light. Samples were left exposed for 29 months in the laboratory environment in a vertical position. Room temperature is usually maintained in the laboratory by means of air conditioning. Samples were exposed to

alternated periods of light and darkness and two types of light sources are present at the laboratory. As sunlight is usually reduced by window blinds, daylight-fluorescent lamps are the main light source. Considering both types of light sources one can assume that the samples were exposed to moderate lighting conditions. Clear window glass cuts out UV radiation below 315nm.[58] The fluorescent lights present emit mainly above c.300nm (see Appendix VII). Besides ordinary fluorescent lamps will emit only 2-6% in the near ultraviolet 320-400nm.[58] Also, the intensity of electric light is 10 to 100 times lower than the intensity of direct daylight.[119] μ-FTIR, FTIR-ATR and colorimetry analysis were conducted periodically on both the samples kept in the dark as the ones kept exposed to light.

Fig. VI. 2: (Right) The set of samples after preparation. (Left) Detail of a sample containing *V7* and *Cenógrafa* white applied over unwashed canvas before aging.

6.1. Results and discussion

6.1.1. Yellowing and the binders

Two binders were chosen the *V7* and the *Sabu Tempera* medium because these emulsions differed in plasticizer content: dibutyl phthalate was detected in the second while its methyl branched analogue diisobutyl phthalate was identified in the first. Being plasticized with DBP *Sabu* was considered to be more similar to the vinyl emulsion found on the studied *White Paintings.* Moreover analysis from artificially aged samples indicated that DiBP had degraded during artificial aging.

The relation between yellowing and the presence of additives is mentioned by Horie as yellowing of films cast from PVAc dispersions occurs far more rapidly than occurs in films cast from PVAc solutions.[120] Moreover recent research conducted by Toja et al. showed that during photo-oxidative ageing DBP promoted a slightly deacetylation of PVAc when compared to films without plasticizer.[74]. Therefore a correlation between the plasticizers and the observed degradation could be tentatively made.

In fact, in terms of color changes samples with *Sabu* showed to be more stable than *V7* paints in all the supports despite being more yellow when freshly applied. (Table VI.1; full results can be found in the appendix VII) Therefore, the instability of *V7* when compared to the *Sabu* might be correlated with the specific plasticizer used. For a full discussion of the results both the Tg and the molecular weight of both emulsions and pigmented samples should be known since phthalates will affect the paint's T_g and therefore influence the physical characteristics of the emulsions and paints. Free volume between chains is reduced by increased molecular weight, increasing the T_g and decreasing chain mobility. If formation of double conjugated bonds depends of intramolecular processes with the formation of membered rings (see Chapter III PVA emulsions: degradation) than the mobility of macromolecular chains is important. Softer emulsions with higher chain mobility should be expected to be more susceptible to photodegradation. With the use of a bulkier phthalate as DiBP than bigger free volume between polymer chains might exist and bigger chain mobility is expected. That might be one of the reasons the *V7* emulsion is more unstable than *Sabu*.

Table VI.1.: L*, a*, b* and ΔE values measured during natural aging in reproductions containing the emulsions *Vulcano V7* and *Sabu* mixed with lithopone.

	***Vulcano V7* + lithopone**			***Sabu* + lithopone**		
Aging time (months)	**L***	**a***	**b***	**L***	**a***	**b***
0	93.91 ±0.04	-0.63 ±0.04	1.59 ±0.06	93.25 ±0.00	-0.64 ±0.04	3.57 ±0.16
6	93.45 ±0.01	-0.92 ±0.01	5.93 ±0.19	93.61 ±0.00	-0.51 ±0.03	4.35 ±0.36
12	92.52 ±0.08	0.48 ±0.06	9.12 ±0.13	93.46 ±0.01	-0.02 ±0.04	3.72 ±0.17
29	90.70 ±0.02	-1.59 ±0.12	14.22 ±0.69	91.87 ±0.49	-0.80 ±0.03	3.79 ±0.09
Δ(L*, a*;b*)	**-3,21**	**-0.96**	**12.63**	**-1,38**	**-0.16**	**0.22**
ΔE		**13.07**			**1.41**	

As in the case studies, μ-FTIR analyzes does not show significant molecular changes that can account for the yellowing of the paints. (Figs. VI.3 and VI.4) Estimation of the relative intensities of absorbance in infrared for the paint samples containing lithopone and calcium carbonate could only be compared in the C-H stretching and ester group vibrations region because the pigment and fillers mask the remaining areas of the spectra. Only the ratio between vCO/vC=O could be calculated within an acceptable experimental error of <10% and all the differences found were within that value. Absorption wavenumbers of C-H groups was heterogeneous since the beginning therefore no conclusions on shifting wavenumbers could be gathered from those differences. Only the areas of the carbonyl band could be assessed within an acceptable error range (Table VI.2)

Table VI.2: Values of peak centre (μ), area (A) and full width at half maximum (σ) calculated by fitting the νC=O absorption with a Gaussian function. The values are the average of three infrared spectra taken from each sample. Spectra were baseline corrected and normalized by the intensity of the C=O absorption band.

		μ		A		σ	
		Unaged	*Aged*	Unaged	*Aged*	Unaged	*Aged*
***V7* + lithopone**	**Glass-slide**	1736	*1737*	24.00 ± 0.44	*24.41 ± 0.37*	24.81 ± 0.59	*24.92 ± 0.24*
	Unwashed canvas	*1737*	*1737*	*24.19 ± 1.48*	*24.82 ± 0.36*	*24.78 ± 0.85*	*25.12 ± 0.37*
	Washed canvas	1737	*1737*	22.99 ± 0.62	*23.25 ± 1.33*	24.32 ± 0.68	*23.95 ± 0.55*
***Sabu* + lithopone**	**Glass-slide**	1736	*1737*	23.92 ± 1.00	*23.12 ± 1.67*	25.07 ± 1.05	*24.20 ± 0.92*
	Unwashed canvas	*1737*	*1737*	*23.46 ± 0.47*	*22.99 ± 1.18*	*24.29 ± 0.32*	*23.89 ± 0.59*
	Washed canvas	1737	*1737*	23.18 ± 1.16	*23.54 ± 1.21*	24.71 ± 0.74	*24.47 ± 0.45*
***V7* + TiO_2**	**Glass-slide**	1737	*1738*	22.54 ± 1.01	*21.92 ± 0.24*	24.40 ± 0.89	*23.33 ± 0.25*
	Unwashed canvas	*1738*	*1738*	*22.47*	*20.51 ± 1.46*	*23.80*	*22.51 ± 0.83*
***Sabu* + TiO_2**	**Glass-slide**	1738	*1738*	23.61 ± 0.97	*22.71 ± 1.28*	24.05 ± 0.63	*23.54 ± 0.67*
	Unwashed canvas	*1738*	*1737*	*22.33 ± 1.81*	*20.53 ± 0.58*	*23.49 ± 0.88*	*22.42 ± 0.46*

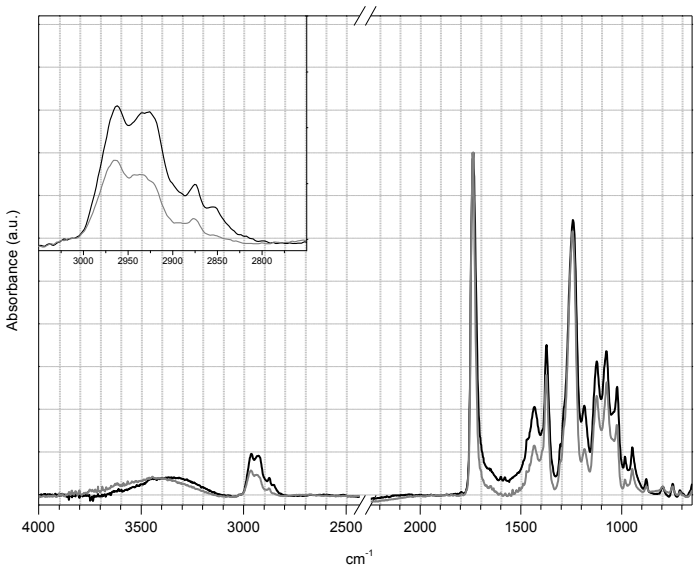


Fig. VI.3. Infrared spectra of the pigmented samples containing the *V7* emulsion and lithopone applied on glass slide before (—) and after (—) 29months of natural aging

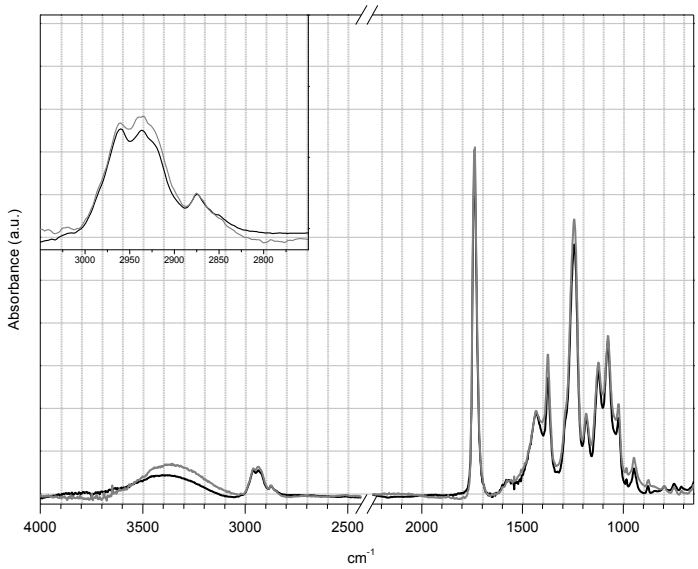


Fig. VI.4. Infrared spectra of the pigmented samples containing the *Sabu* emulsion and lithopone applied on glass slide before (—) and after (—) 29 months of natural aging

6.1.2. Yellowing and the pigments

Both binders were mixed with the *Cenógrafa* white and TiO_2 (rutile form) in order to assess the pigments role in yellowing. Most of the paints' containing lithopone had higher initial b* values than paints containing TiO_2. The range of b* was of: 1.59-3.80 for the set of *V7* plus lithopone; 5.09-3.57 for the set of *Sabu* plus lithopone. A range of 2.81-3.34 was measured for the set of both binders mixed with TiO_2. (see Fig. VI.5 and Appendix VII) The differences between the pigments can be due to the higher reflectance and opacity of rutile which has a higher refractive index (n_D=2,73 [61, 102]) than zinc sulphide (n_D =2.37 [1, 102]).

According to the results titanium dioxide is acting as stabilizer (similarly to what happened in artificial aging) while the lithopone/calcium carbonate mixture is sensitizing its degradation. Pigments can act as stabilizers by either reflecting and/or absorbing the damaging incident light [61] or, they can absorb light and pass that energy into the polymer decreasing the polymer's resistance. While modern coated rutile TiO_2 is known for its stability, it should be noted as was previously discussed that ZnS is a photo-catalytic pigment.[44] In fact, there is a strong shift in lithopone's absorption band towards the blue (UV-A region) and this pigment is especially useful as a white pigment for UV-cured paint films.[102] Also, zinc sulphide is being used as an alternative method for the removal of organic pollutants from water because it is a semi-conducting material and therefore is capable of mediating photocatylic oxidation of organic compounds of materials.[121] Charge transitions in the conduction band of ZnO occur in its excited state and the electron in its conduction band is transferred to molecular oxygen leading to the formation of a series of radicals.[121]

As expected the pigment and/or filler is playing a significant role in yellowing as the paint's behavior could be divided in two main groups: rutile and acrylic gypsum containing paints where

minor changes were measured; and, vinyl paints made with lithopone which showed significant yellowing.

L* values do not seem to be significantly affected. Unaged paints made with the titanium white were slightly lighter than the samples containing lithopone. After aging the values for all the samples show a tendency to become slightly darker (Fig. VI.6, full results are shown in Appendix VII)

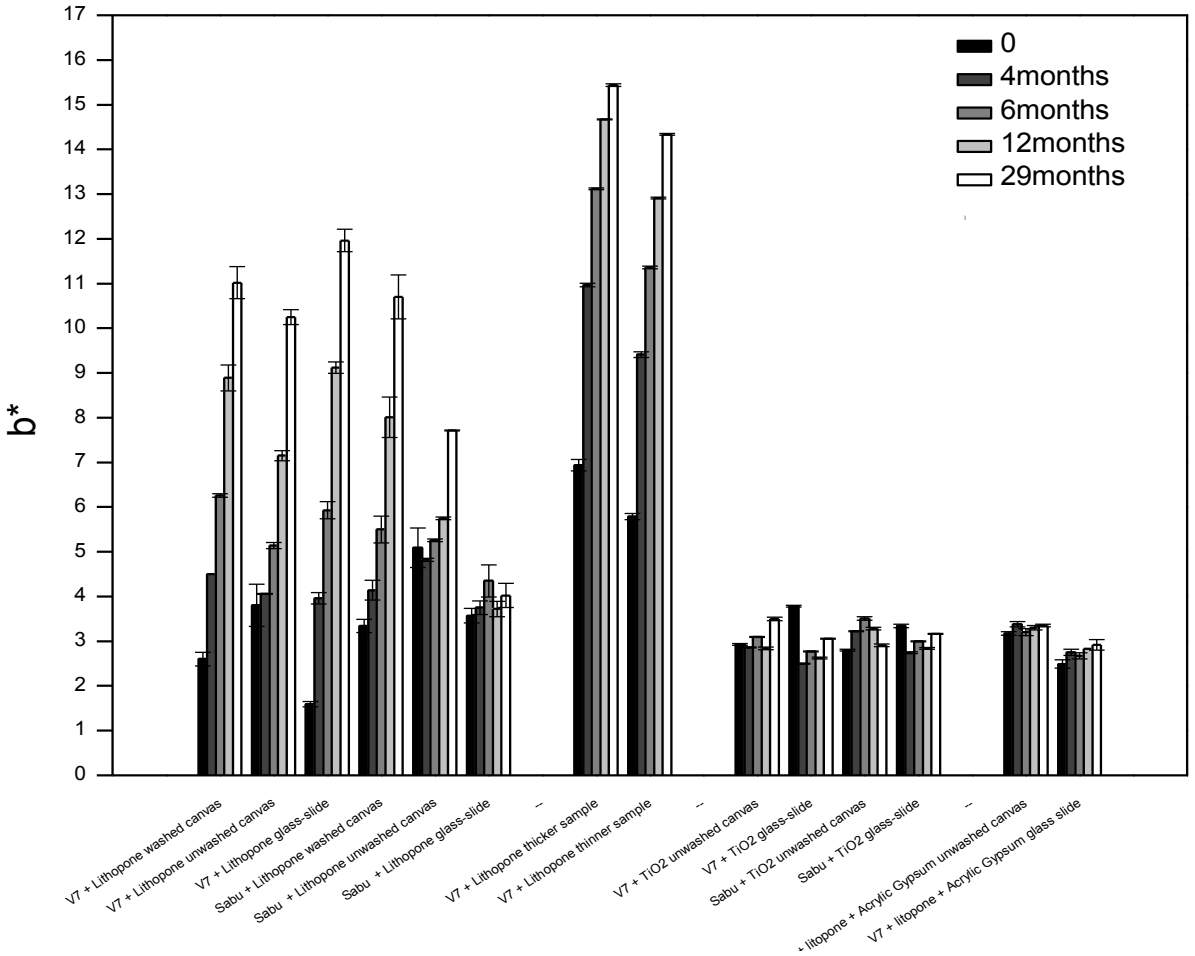


Fig. VI.5. Graphic depicting the b* values measured on samples subjected to natural aging during a total of 29 months.

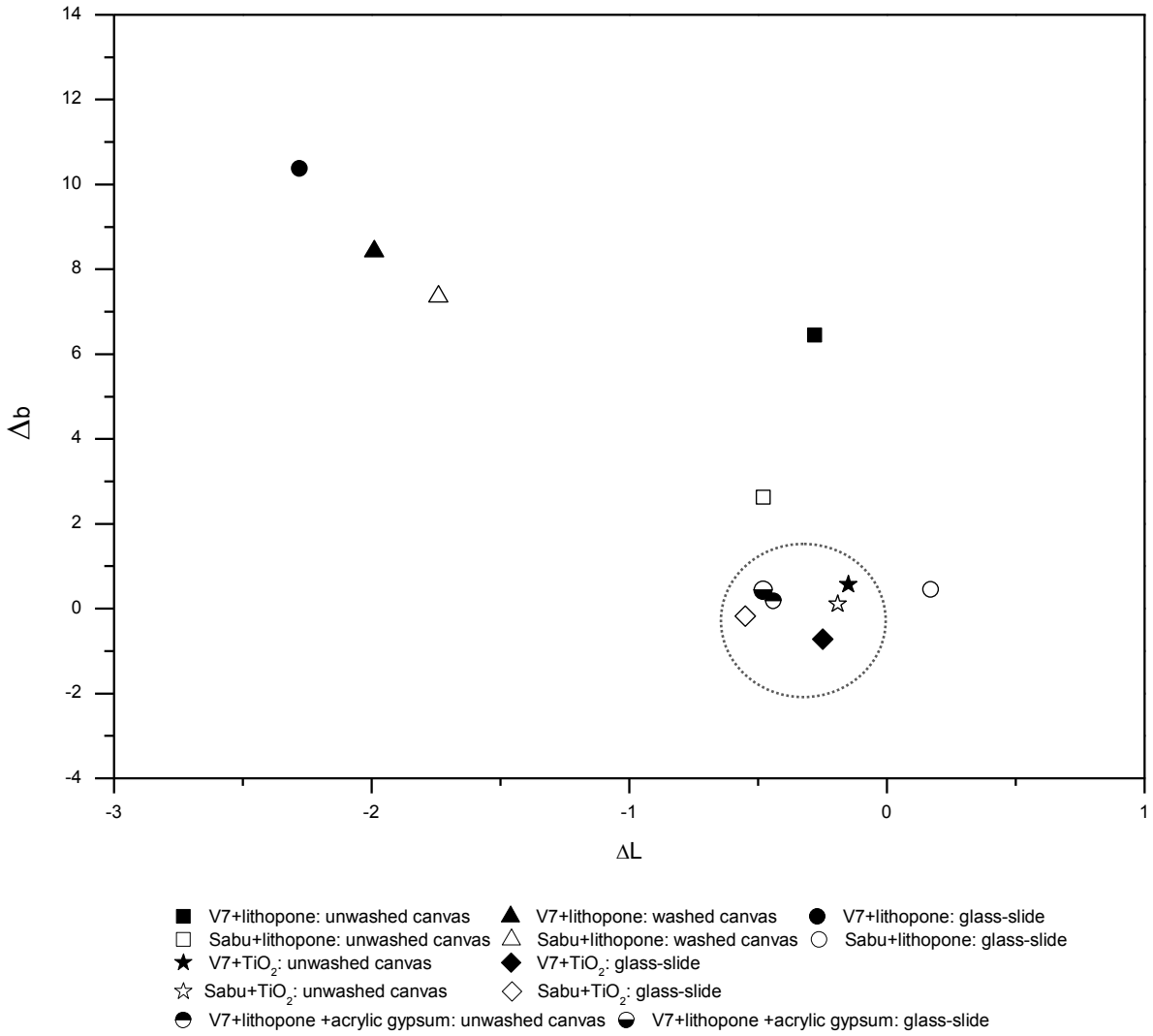


Fig. VI.6: ΔL* and Δb* after 29 months of natural aging

6.1.2.1. Diffuse reflectance spectra

In some studies where yellowing of PVAc was observed the characteristic stretching vibration absorbance at 1650-40cm^{-1} resulting from unsaturated groups was not detected.[63,69] However absorption at lower wavelengths were detected using reflectance spectroscopy and are usually attributed to the formation of conjugated double sequences.[62] UV absorption values of conjugated double bonds can be found in the literature and the level of conjugation has specific absorbance values: maximum levels in the range from 230nm up to about 400nm corresponds to conjugation lengths of n=7; absorbance values at 273nm correspond to n=3 [62]; and, absorbance values at 375nm are attributed to n=5 [122]. Presence of polyene sequences formed during irradiation of PVAc was been ascertained through the development of absorptions in UV spectra of degraded samples: at 295nm [63] or at 272nm [69]. Authors attributed the lack of detection of these groups by FTIR to the low absorption coefficient of those degradation products [63,69]. Polyene sequences in PVAc irradiated samples studied by Kaczmarek and Halina showed an UV absorbance at 275nm. A small increase of absorbance between 300-400nm indicated, according to the authors, the development of new chromophore groups like shorter polyenes and saturated and unsaturated ketone groups. However, in this case there was no coloration of the pure PVAc samples.[70] The photodegraded PVAc studied by Buchanan showed an absorption at c.272nm in the UV spectra that authors ascribed to the formation of polyenes. Infrared spectral changes revealed the loss of acetate side groups however there were no infrared bands related to unsaturation.[67] Increase of absorbance (without any structured absorption maximum) in the range 400-800nm in the UV-visible spectra of yellowed PVC/TiO_2 paint samples was been attributed by Gardette and Lemaire to the formation and accumulation of polyenes and accounts for yellowing of the samples.[50] Another example can be seen in the formation of unsaturated groups in PE as was detected by UV absorption spectroscopy: Gamma irradiation and thermal aging of ethylene-vinyl acetate-vinyl alcohol (EVA-OH) terpolymers resulted in a yellowed material due to the appearance of conjugated double bonds absorbing between 350-380nm and at 375nm.[122]

As no differences could be detected with µ-FTIR, reflectance spectroscopy was performed in some of the yellowed samples. Reflectance and absorbance spectra of the raw components, emulsion and pigment/filler have already been showed. Absorbance spectra of unaged and discolored samples is show in Figs.VI.7 and VI.8. For *V7* + lithopone (the most yellowed samples) the difference between spectra relies in a difference of the photoluminescence intensity and a slight shift in the discolored samples towards longer wavelengths. Although no well-defined maximum could be distinguished subtraction of the absorption peak between unaltered and discolored paint samples revealed that new species might have formed and absorb between 533nm and 539nm. Besides this general trend other new species absorbing at lower wavelengths are detected. Severely yellowed *V7* + lithopone after 17 months of exposure showed the formation of new small bands absorbing at circa: 370nm, 384nm and 405nm. Also the absorbance at 362nm present in the unaged sample and attributed to the phthalate plasticizer disappears in the yellowed sample. *Sabu* + lithopone after 17 months of exposure show the formation of two new small bands

absorbing at circa: 382nm and 358nm. Also the absorbance at 368nm present in the unaged sample and attributed to the phthalate plasticizer disappears in the aged sample. These values seem to be in accordance with the values of published literature described above.

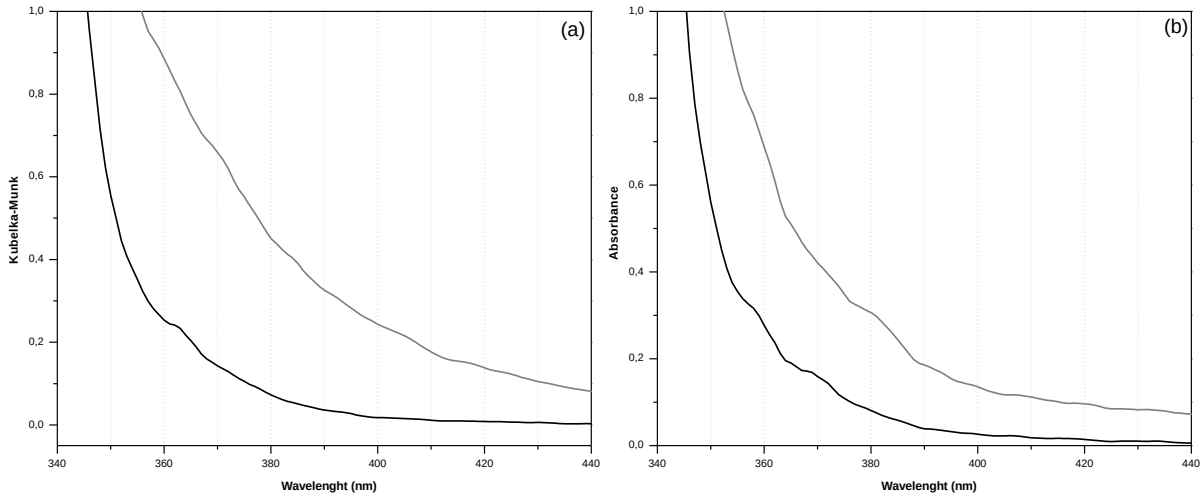


Fig. VI.7: (a) Absorbance spectra of *V7* + lithopone over glass-slide unaged (—) and aged for 17 months (—).
(b) Absorbance spectra of *Sabu* + lithopone over glass-slide unaged (—) and aged for 17 months (—).

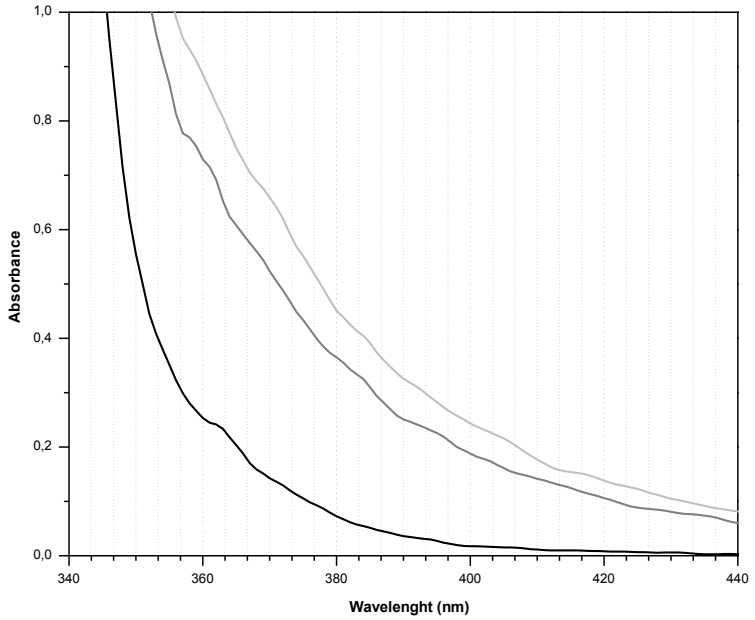


Fig. VI.8: Absorbance spectra in the 340-440nm range of *V7* + lithopone over glass-slide unaged (—) and aged for 17 months (—), *V7* + lithopone over unwashed canvas aged for 17 months (—).

6.1.3.The cotton canvas support

Because Sarmento claims that no size is applied over the canvas there was concern that paint's yellowing might be related to the cotton textile. This effect of the support on the yellowing of paints, usually designated *support induced discoloration* has been studied by other research groups. Hamm et al. have observed that acrylic media directly applied over cotton canvas yellowed when exposed to natural environmental conditions. His research showed that a support induced

coloration occurred quite rapidly in a brief period of time and that washing the fabric markedly reduced the yellowing of the acrylic media. The mechanism presented by the authors was solubilization of the finishing materials used in the cotton by the water in the paint's emulsion, followed by migration of these substances to the surface during paint drying.[123] Research conducted by Ormsby et al. gave similar results. *Talens* white paints applied on cotton canvas and kept in the dark for 42 months showed increased yellowing when compared to the equivalent free films.[93]

Textile treatments and finishing include chemicals that change the fabric's aesthetic and/or physical properties and a comprehensive review was written by Tomasino.[124] Sizing the fabric involves coating the fibers surface with a water soluble, film forming substance (either alone or, in blends) e.g.: starches, polyvinyl alcohol, (the two most often used) gums, carboxymethyl cellulose, dextrine, polyacrylic acid, gelatin and other synthetic polymers. Other ingredients are typically added to optimize the process e.g.: lubricants (oils, fats and waxes); humectants (glycerine, ethylene glycol, urea); and, preservatives (cresol, phenol, salicylic acid). Other finishing products include softeners (hydrocarbons), repellent products (like paraffin waxes or, polysiloxanes) or, flame retardant finishes (for example, sodium borate).[124]

A raw cotton canvas used in the 90's was provided by the artist and was used for testing. The same paints were also applied over glass-slides to be used as reference samples. Unwashed canvas was used directly while washing was carried out several times with warm distilled water. Results of the characterization and washing of the cotton canvas are presented in Appendix VI: Natural aging. µ-FTIR analyses showed that the water soluble material extracted during the washing was composed mainly of a starch based product. However evidence of a blend with a cellulose derivative (e.g. carboxymethyl cellulose) was also found. Infrared spectra of washed and unwashed canvas indicated that a significant amount of the yellowed colored finishing products was removed with washing. µ-XRF analyses also indicated that washing was efficient for removal of some of the metallic ions present in the canvas.

Yellowing is uneven regarding the supports. For the *Sabu* samples the fact that the paint applied over canvas (both unwashed and washed) yellows more than paints applied over the glass-slide does suggests a support induced discoloration, although no migration of the finishing products was detected. On the contrary *V7* white paints on glass-slides yellowed more than the corresponding paints applied over canvas. Both results indicate the higher stability of the *Sabu* when compared to the Vulcano and apparently the intrinsic instability of the *V7* white glue when mixed with lithopone.

The measured initial b* values of the samples were as expected. Paints applied on the unwashed cotton canvas have higher b* values than paints applied on washed canvas and glass-slides due to the influence of the support's yellowish color. (Fig. VI.5)

However, an important conclusion could be drawn from the paints with TiO_2 over unwashed canvas. After 17 months of exposure differences in infrared spectra were noted and are related to solubilization and impregnation of the paint with the canvas finishing products. (Fig. VI.9) The appearance of the O-H stretching band at 3365cm^{-1} and of the C-H stretching band at 2940cm^{-1}

could be related to the starch. Unexpectedly these paints retain their white color. (See Figs. VI.5 and VI.6)

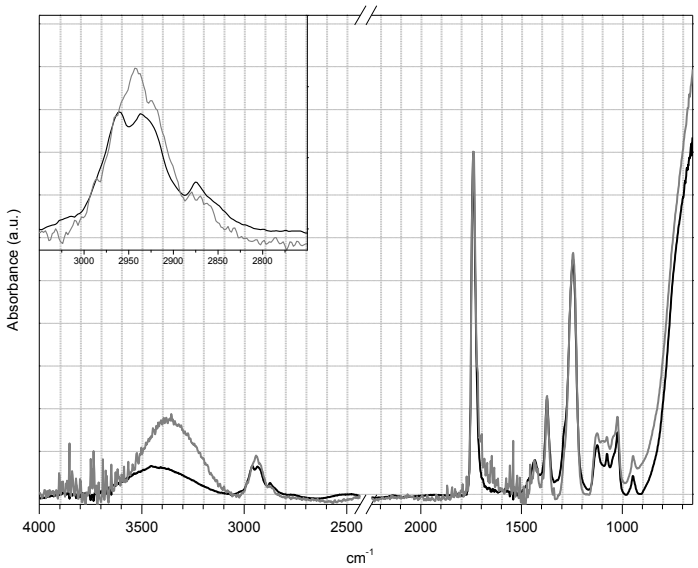


Fig. VI.9. Infrared spectra of the pigmented samples containing the *Sabu* emulsion and rutile TiO_2 applied on unwashed cotton canvas before (—) and after (—) 29months of natural aging.

6.1.4. Paint discoloration and paint thickness

A set of samples was used to evaluate the influence of paint layer thickness. Data obtained from this set shows that the b* value is influenced by the paint layer thickness. After more than 17 months of exposure to ambient conditions the thicker sample is slightly more yellow (b*=15.44 ±0.03) than the thinner sample (b*=14.34 ±0.02). This means that discoloration is proportionally dependent to layer thickness as also been noted by Whitmore, Colaluca and also by Hamm.[84,123] Nagai et al. studied the degradation profile of several synthetic polymers subjected to UV-irradiation and concluded that there is an accumulated layer of degraded species that functions as a self-barrier effect that will absorb UV irradiation more strongly and disturb the penetration of UV light to the inner part of polymers.[125] Also, the rate of oxygen absorption in a film is diffusion-controlled and the rate is linearly proportional to the film thickness.[59] That might explain why the yellowing degree was the same for both samples: Δb*=8.50 and 8.55 for the thicker and thinner paint samples respectively.

6.1.5. Exposure to dark and reversibility of color changes

In some cases paint discoloration can be reversed by removing the exposure conditions that caused yellowing. Yellowing of an acrylic waterborne emulsion that occurred during storage in the dark was reversed with a brief exposure to high-intensity visible light although after subsequent dark storage the discoloration returned.[126-127] The same experiments carried out in support induced discolored binding media gave less satisfactory results.[126-127] Similar results were obtained in other brands of acrylic based emulsions with the additional finding that exposing the samples to light/dark intermittent exposures prevents yellowing of the films when compared to the

same films kept in the dark.[126-127] Another example of light bleaching is mentioned for PVC samples. Discolored poly(vinyl chloride) films kept in dark storage were bleached with light exposure.[50] As has been mentioned in this particular case bleaching was attributed to the photoxidation of polyenic sequences when exposed to oxygen.[50]

Natural aging of a mock-up created by Sarmento himself during the workshop held at the DRC was followed during storage in the dark and when exposed to light. The binder/pigment ratio follows the trend used in the paintings from the 90's. The base emulsion used is a PVAc with glycol benzoates type plasticizers (*Bizonte* white glue). This mock-up was used to evaluate the role of light and/or oxygen in the paint's tendency to become yellow and on the possibility of reversing the process. The reproduction has stored in a k-line custom made box that was periodically opened for analyzes to be conducted. The sample was kept in the dark for approximately 24months. Because no differences in color were detected after 8 months of being stored in the dark, a fragment of 36cm by 6cm was cut down and exposed in the laboratory to the ambient conditions described above. The fragment was exposed to light for approximately 16 months.

Visually it was possible to see that yellowed areas of paint appeared during exposure to light in ambient conditions. Discolored areas seemed to be restricted to where more paint had been applied. Colorimetry values between the exposed and unexposed samples do not differ significantly. After 16months of light exposure the paint presented values similar to sample the sample stored in the dark. That was due to the difficulty of measuring the values in flat areas of the paint. As the sample kept in the dark remained white, suggesting that the storage conditions used (either absence of light or, of oxygen) were preventing the paint from being discolored a fragment from that yellowed sample (exposed to light) was re-stored in the dark. Moreover this experiment would reproduce the process used in a museum where after being exhibited the painting would be stored in the dark. After a few months of being kept in the dark colorimetry values showed that the sample continued to yellow. The process was not reversed and moreover was continuous.(Table. VI.3)

Table VI.3. L*, a*, b* and ΔE values measured during natural aging in the reproduction done by Sarmento with *Bizonte* and *Cenógrafa* white apllied on an unwashed cotton canvas.

	Kept in the dark			**Exposed to light**			**Back in the dark**		
Time (months)	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***
0	**91,15 ±1,68**	**-0,05 ±0,23**	**3,92 ±0,31**	**91,48 ±1,43**	**-0,02 ±0,30**	**4,16 ±0,34**	**91,60 ±0,87**	**-0,87 ±0,11**	**10,76 ±1,57**
12	**91,48 ±1,43**	**-0,02 ±0,30**	**4,16 ±0,34**	**91,60 ±0,87**	**-0,87 ±0,11**	**10,76 ±1,57**	**90,24 ±0,66**	**-0,83 ±0,04**	**13,47 ±0,58**
Δ(L*. a*; b*)	**-0,04**	**0,01**	**0,02**	**-0,12**	**-0,85**	**6,60**	**-1,36**	**0,04**	**2,71**
ΔE		**0,05**			**6,66**			**3,04**	

Fig. VI.10: Detail of the workshop sample. The right side was kept in the dark and the left side was the cut fragment that was exposed to light showing yellowing of the paint layer.

A note on Artificial aging vs natural aging

In terms of yellowing artificial and natural aging occurred at different rates being faster in the latter case. There are to many considerable differences between the conditions of the two experiments in order to be able to identifiy a specific reason.

As discussed earlier photoxidation reactions and rates depend on the irradiation wavelength.[56] For example, Pablos et al. studied the photodegradation of polyethylene films under natural outdoor ageing and artificial ageing (300-800nm) and although the same photodegradation trend was established (oxidation and chain scission) samples under artificial ageing suffered a higher degree of degradation as a consequence of the higher total radiation.[128]

Feller mentions that fading of alizarin lake and other artists' oil paints exposed to daylight fluorescent lamps daylight was higher when alternate periods of light and darkness were employed.[58] If there is a "dark reaction" in any system then it should be obvious that alternating conditions will result in a different net degree of change.

Additionally, other authors defend that further exposure conditions like temperature and humidity can give rise to different behaviors.[58] Water can have at least three different but important effects on polymer degradation . One is chemical: hydrolysis of the ester or amide bonds. The second is physical: loss of the bond between the vehicle and a substrate or pigment. The third is photochemical with generation of hydroxyl radicals or other chemical species. The high intensities of illumination employed in accelerated testing often raise the temperature of the

samples and may also lower the samples' moisture content.[58] Moreover, discontinuous exposure, that is, exposure under alternate conditions of light and dark, may produce results that are different from those obtained under continuous exposure. Under these conditions the samples cool down when the lights are turned off resulting in a buildup of moisture content.

Another difference to take into account is the polymer chain mobility during both experiments. In the Solarbox higher temperatures might have been reached than under natural aging conditions. If the rate of deterioration is dependent upon the presence of oxygen and the rate of deterioration is governed principally by the diffusion of oxygen chain mobility and free volume are important and determine the diffusion of molecules through the bulk of the polymer.

Besides the external conditions the samples used in both experiments were diferent. In the natural exposed samples a ratio of binder pigment of 70-30% was used while in the artificially aged samples a ratio of 45 - 55% was used.

6.2. Conclusions

Natural aging seemed to reproduce the natural discoloration claimed to be hapening in the studied Sarmento's paintings and it can also be correlated with the artificial aging results.

All samples, despite exposure conditions, thickness or support that contain TiO_2 as a colouring agent showed to be more stable. That is in agreement with all the results described so far as this pigment is effectively stabilizing the polymer. Changes in colour in these samples is negligible. The migration of some finishing products from the canvas might be related with the consistency of the paint prepared with this pigment. The paint was in a more fluid state and that might have prompted the diffusion and migration of the water soluble finishing products present in the cotton canvas. The coating of acrylic gypsum apllied on top of the PVAc + lithopone pigment reveals a similar behavior. Yellowing did not occur in this samples.

Similarly to artificial aging lithopone did not have a significant stabilizing effect on the polymer all samples containing *Cenógrafa* white yellowed after c. 2 years of exposure to light in ambient conditions. When compared to artificial aging the yellowing difference is significant achieving ΔE values of 10 to 13, values that are much closer to the values measured in Sarmento's paintings.

Between the *V7* homopolymer containing DiBP and *Sabu* homopolymer containing BDP it seems the first yellows more than the later. Further analysis could be used to elucidate if there is a direct relation with the phtahalate content and the properties it imparts to the paint layer, namely, chain mobility and oxygen permeability. Furthermore Py-GC/MS analyzes could elucidate if DiBP is already degradading after a few years of exposure. The unevenness of the results obtained with the diferent substrates make it difficult to correlate them with the yellowing differences. However, the results obtained with the samples containing TiO_2 sugest that even if there is a migration it might not have a significant impact on the yellowing of the white paint layers.

The yellowing seems to be irreversible. Placing an already yellowed sample in the dark in a closed container did not reverse the process. The samples continued to yellow.

— Part II —

Cleaning synthetic paints: preliminary findings and future research

1.1. Introduction

Cleaning of contemporary paintings has been an issue of concern for conservators world-wide. The paint's low T_g makes the surface prone to damage and to imbed dust and dirt. Moreover, additives that migrate and stay deposited on the surface increase affinity for dirt pick-up. Practical knowledge acquired through treatments typically applied to paintings created with traditional binders and results from research done in that field cannot be applied directly in the treatment of contemporary paintings. Not because the products *per se* might not be the right ones but, because we do not know how the products used can affect synthetic paints. Synthetic paints typically include a complex mixture of additives that are likely to influence the paint's response to different treatment methods. For instance, even if synthetic paints are known to be insoluble in water after drying, water-soluble components used to stabilize the suspended polymer in the liquid paint might remain in the dried film. Therefore, although the binder in itself is not soluble in water some of the paint's components might still be water sensitive making the film permeable to water. Moreover, chemical, morphological and physical properties changes can be induced by the solvents used.

Main treatment concerns and research findings for acrylic paints have been listed by Learner and Ormsby and include: swelling of paint films, extractable components and surface changes due to use of organic solvents and aqueous systems for surface cleaning.[129] Resistance of commercial colored vinyl paints towards solvents was been assessed by Doménech-Carbó et al. and results show that immersion in water (from 10 minutes to 12 hours) provokes dissolution of additives and that for longer exposure times the polymer lattice can also be affected. Consequently the mechanical properties of the paints can be affected as the paint films get more brittle.[130] Immersion of PVAc based commercial paints by Doménec-Carbó et al showed that the aqueous extracts contained a nonionic polyethoxylate surfactant and a cellulose ether-type thickener.[130]

One of the focuses of this research was to determine the consequences that arise from cleaning polyvinylacetate paintings so that conservators-restorers would be able to make more informed treatment decisions. However, this is only possible by studying the vinyl based paint components, the properties of the paint films and the long term aging effects. Surface cleaning effects can only be better understood once a broader knowledge is established. However, due to the formulation (e.g. the presence of several additives) of synthetic paints the subject is vast and complex. Therefore although only preliminary results were obtained they do point to some of the vulnerabilities of these paints' towards aqueous and organic solvents and are helpful in establishing priorities for future research. Two types of samples were studied to asses vinyl paints behavior towards cleaning methods. Both contained the homopolymer emulsion *Vulcano V7* together with a white pigment, either titanium white or, lithopone plus calcium carbonate. The set containg TiO_2 had been subjected to accelarated aging while the set containing lithopone had been naturally aged.

1.2. Cleaning acrylic paints: subject review

Research on the cleaning of acrylic paints has been conducted mainly on commercial artist's paints (*Winsor&Newton*; *Talens*; *Liquitex* and *Golden*) containing either polybutyl acrylate/methyl methacrylate p*n*(BA/MMA) or, ethyl acrylate/methyl methacrylate p(EA/MMA). Pigments studied range from inorganic (titanium white, burnt umber, cadmium yellow, cadmium red, cobalt blue, Mars red and black, chromium oxide) to synthetic organic ones (PY3 azo yellow, phthalo greens PG7 and PG36, PV19, PV23, PR122, PR207). The fillers studied were chalk, barium sulphate and calcium sulphate. Samples from new, artificially aged (light and thermal aging) and case-studies (naturally aged paintings) have been studied.[131-134]. To assess the effect of commonly used cleaning products and methods, the wet cleaning systems chosen included aqueous solutions and hydrocarbon solvents: distilled or deionised water; pH adjusted water (with a minimum pH value of 4.5 and maximum pH value of 11); Triton X-100/XL-80N; triammonium citrate; ethanol; adjusted solutions with salts (to chosen values of pH, conductivity and ionic strength); Stoddard and Shellsol solvents.[131; 133] Paint's behavior was followed by immersion in the cleaning solutions and solvents. In a more realistic approach cleaning simulation was also conducted by using cotton swabs with a time of application ranging from to a few seconds to 1min.[131]

Extraction of soluble components when cleaning acrylic paintings is one of the main conservation concerns. One of the outcomes of the Acrylic Paints Research is that with time there is exudation of the emulsion surfactant to the surface of the paint layers which can be removed with aqueous treatments.[135;136] Paint brand, pigments and aging influence the amount extracted. Prolonged exposure (from 1 to 24h) to aqueous systems results in the extraction of a non-ionic surfactant from the bulk paint film [131; 134] and 5-10s or, 20s of swab rolling is enough to remove surfactant deposited in the paints surface. [131;132] Extraction studies have demonstrated that the extraction rate is greatest within the first 5 minutes.[134] The extent to which the surfactant is extracted from bulk paint films depends on: pigment present, e.g. synthetic organic and iron-based pigments are relatively difficult to disperse in the emulsion therefore bigger quantities of surfactant are needed [132]; age; and porosity.[129, 131] An important finding is that removal of surfactant occurs with several aqueous–based cleaning systems however there is no removal of surfactant when non-polar aliphatic solvents are used [131; 132; 135] when this occurs with this solvent it is usually attributed to the mechanical action of the cotton swab. Also there is no evidence that the addition of surfactant or, chelating agents to the water has any additional influence on surfactant removal.[135] Another Important finding is that there is continuous exudation of this additive to the paint's surface after treatment.[135]

Acrylic paints are easily swollen with aqueous cleaning systems and can dissolve in most organic solvents (for example, ethanol and acetone). Non-polar hydrocarbon solvents (mineral spirits or, white spirit) cause the least swelling.[133] Unfortunately, these are poor cleaners. Paints vary in terms of the amount of water-extractable materials which in turn has significant influence on swelling response.[129,131] Paints with higher medium and surfactant content tend to swell more. [129,131] Thermally aged samples tend to swell less.[129,131] Light aged paint films (≈50 years of

exposure under normal museum conditions) swell less than the equivalent unaged paint samples.[133] This effect has been attributed to the loss of surface and bulk surfactant in the aged paint film. Films containing synthetic organic pigments swell more than the corresponding inorganic pigment paint films.[133] This has been attributed to the bigger surfactant quantity needed to suspend this hydrophobic pigments in the paint emulsion and also because they have typically high tinting strength there will be less pigment and more binder in the paint.

There is also concern as in terms of how cleaning may affect the mechanical properties of acrylic paintings. Research has show that acrylic paints become less flexible after treatment.[136] T_g increases when samples are aqueous treated and exposure time influences the degree. If the exposure to water is short the changes in the tensile properties of the bulk film are negligible. Nevertheless strength and stiffness values have increased uniformly after the surfactant leaching [129, 131, 134] Interestingly the low-aromatic mineral spirit results in only small changes independent of exposure time.[132; 136]

Paint sample's morphology may alter when subjected to treatment. Paint surfaces can become slightly rougher after aqueous swabbing treatment and the final roughness of cleaned films is partially dependent on the amount of surface surfactant present.[129,131, 137] An increase in the number of surface pores, some surface disruption and possible pooling of organic material has been noted in same analysis particularly after the use of organic solvents.[129, 131, 137]

In terms of color and gloss changes due to cleaning no significant color change has been reported as a result of aqueous swabbing systems.[132] However, they cause small changes in surface gloss as a result of the removal of dirt and/or of the deposited surfactant that is exuding to the surface.[132]

Some studies mention pigment and/or filler removal. The presence of barium sulphate was detected in the water extract of an orange paint from the Jeremy Moon's painting *Untitled 2/72* (1972).[132] Calcium sulphate was detected in the water extracts of the dark purple and violet colors of the Alexander Liberman's painting *Andromeda* (1962).[132]

The research conducted so far shows that the changes occurring with aqueous treatments are relatively minimal considering the bulk of the paint films despite the extraction of soluble components e.g. the surfactants.[129;131; 135]

1.3.PVAc emulsion paints: cleaning concerns

Although PVAc dispersions are insoluble in water after drying the polymer matrix can be swollen by water, becoming opaque white but, reverting to a clear film on drying [120]. Furthermore PVAc films can be affected by common organic solvents as can be seen in Fig. I.1.

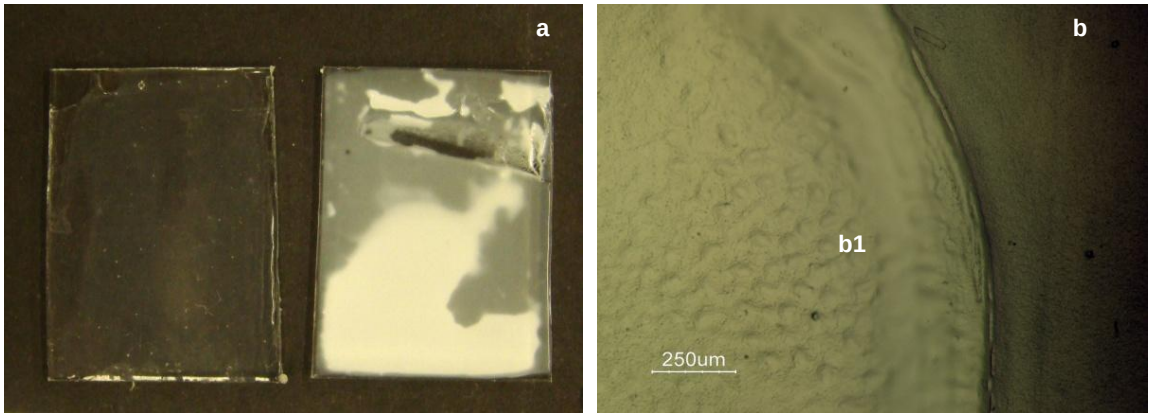


Fig.I.1.: a) Image of the incorporation of water in a pure vinyl emulsion film. The sample on the left is untouched. The sample on the right was immersed in water. The opaque color indicates the polymer was swollen with water.b) Image taken on the microscope of a similar film after contact with a drop of ethanol. (obj.10x, reflected polarized light). b1) area where the drop was deposited after drying

Pigments may affect the resistance towards water cleaning methods. For example, carbon blacks are normally hydrophobic however they have a high affinity for aliphatic and particularly aromatic hydrocarbon solvents. Paint additives may also play a role in cleaning consequences. In the case of the plasticizers because phthalates are hydrophobic organic liquids their water solubility is low: DiBP has a solubility of 20mg/l and DBP 11.2 mg/L.[22] Research in the plasticizer industry seeking the reduction of plasticizer leaching and migration showed that plasticizer extraction from the polymer surface is a successful method to reduce diffusion and leaching.[24] After being briefly exposed to solvent and left to dry the polymer surface is left with a heterogeneous plasticizer distribution and a rigid surface that blocks interfacial mass transfer of the polymer.[24] Besides, the stabilization of PVAc dispersions with protective colloids such as poly(vinyl alcohol) and cellulose derivatives influences the water resistance of the films.[1] These products are water soluble and can therefore be removed from the paint. Extraction of water soluble material from commercial colored artist's paints after 24 hours immersion in distilled water was studied by Silva et al.[17] Styrene and poly(ethylene glycol) (PEG) -type surfactants were found on the extracts.[17] The PEG-type surfactants are responsible for the hazing affect on acrylic based paints and are water soluble.[138]

Polymers that contain functional groups that are sensitive to water like esters can suffer from hydrolytic degradation. De-esterification with the formation of acids and the original glycol are the main products.[61] It is known that hydrolysable ester linkages present in PVAc can be affected by alkaline water (pH≈13) leading to the formation of a free carboxylic acid (acetic acid) while the remaining side chain will end with a hydroxyl group (poly(vinyl alcohol).[139]

The polymers used also play a significant role in the water resistance. For instance for copolymers of PVAc and PE the water permeability increases as expected with the VAc content as there will be more polar groups in the polymer matrix. However blends of EVA with PVC show a decrease of permeability to water due to the glassy nature of the PVC polymer.[76]

1.4. Observations of the behavior of vinyl white paint in solvents: the starting point

During trials for the removal of the glass fragment from *Inadequate Readings* (see Appendix VI, Conservation treatment of *Inadequate Readings*) some solvents were tested namely, distilled water and ethanol. Previous experiments had showed that although these two solvents might not provoke the dissolution of the film they do seem to affect the surface morphology. (Fig. I) In the case of the treatment trials after application and evaporation of both solvents the surface was left with a shinny appearance. Therefore, some tests were run under a stereomicroscope to assess differences in the surface. A drop of both solvents was applied in the same paint reproductions used in treatment trials and left to dry. The distilled water used had a pH of ≈5. Ethanol was of commercial pure grade. (Figs. I.2 and I.4)

The same shinny deposit seen previously was detected in both cases. Moreover, ranking light on the paint subjected to water showed the surface was disrupted and in the case of ethanol the substance was preferentially deposited along the limits of the ethanol drop. Several micro samples taken from both cases were analyzed by µ-FTIR.

Infrared spectra of the deposit formed due to contact with water shows poly(vinyl alcohol). (Fig. I.3) As it has been mentioned PVAl is a common protective colloid in vinyl emulsions and is water soluble. In the case of ethanol the infrared spectra of the deposit (Fig. I.5) shows it is made of pure poly(vinyl acetate) and phtahalate. That indicates that both binder and phthalate plasticizer were dissolve when in contact with ethanol. In the case of the phthalate that could be expected because it has low solubility in water, however DBP is soluble in ethanol. Also PVAc, is soluble in ethanol.

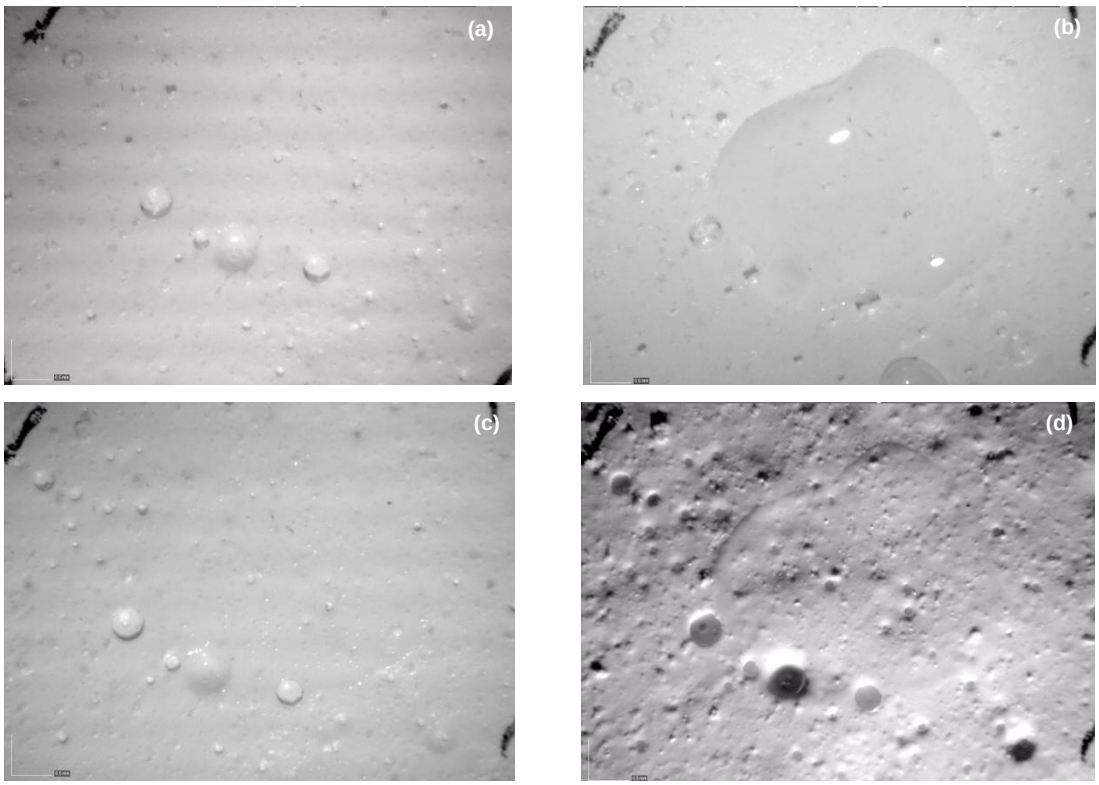


Fig.I.2 : a) Image of the paint surface under the stereomicroscope (obj. 11x, reflected light) before application of water. b) drop of water. c) image after water evaporation. d) the same image under raking light

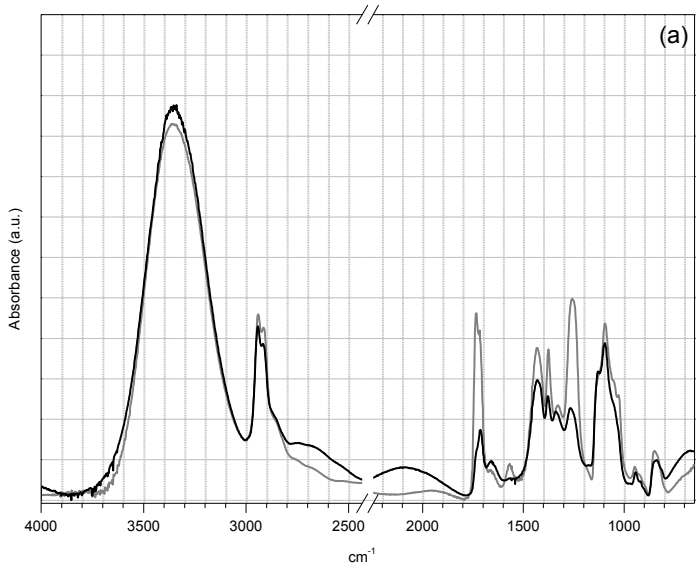


Fig.I.3: Infrared spectra of the deposit left on the paint's surface after exposure to water.

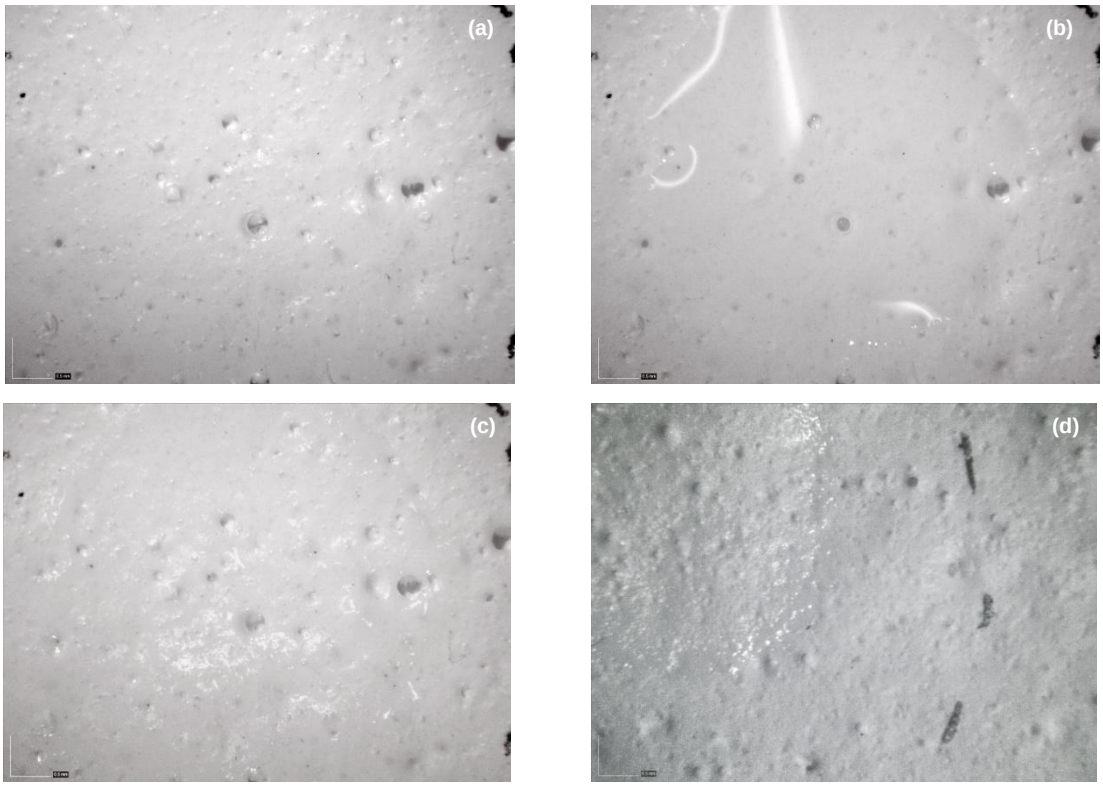


Fig.I.4 : a) Image of the paint surface under the stereomicroscope (obj. 11x, reflected light) before application of ethanol. b) drop of ethanol. c) image after ethanol evaporation. d) detail of the limits of the drop under raking light.

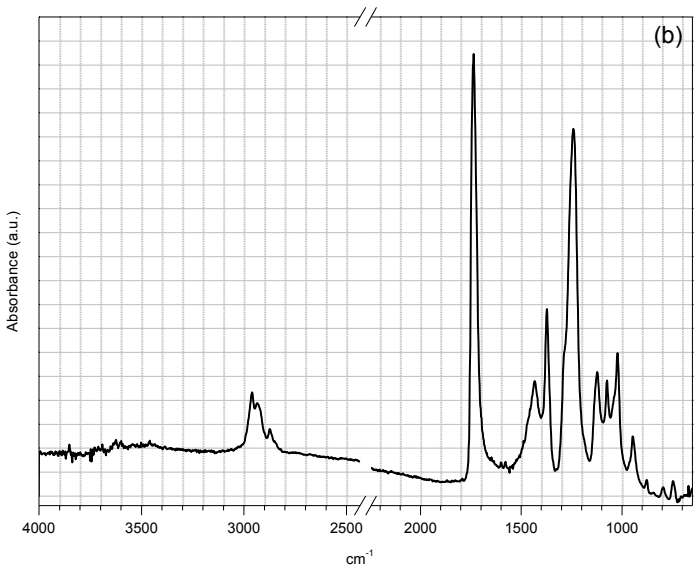


Fig.I.5 : Infrared spectra of the deposit left on the surface after exposure to ethanol.

An important observation regarding paint aging and its behavior towards water should be made. Aging makes the paint more resistant to water as can be seen by immersion of *V7* and lithopone samples in water: with unaged film a milky dispersion is formed; while artificial aging reduced increasingly the ability to suspend the polymer.(Fig. I.3)

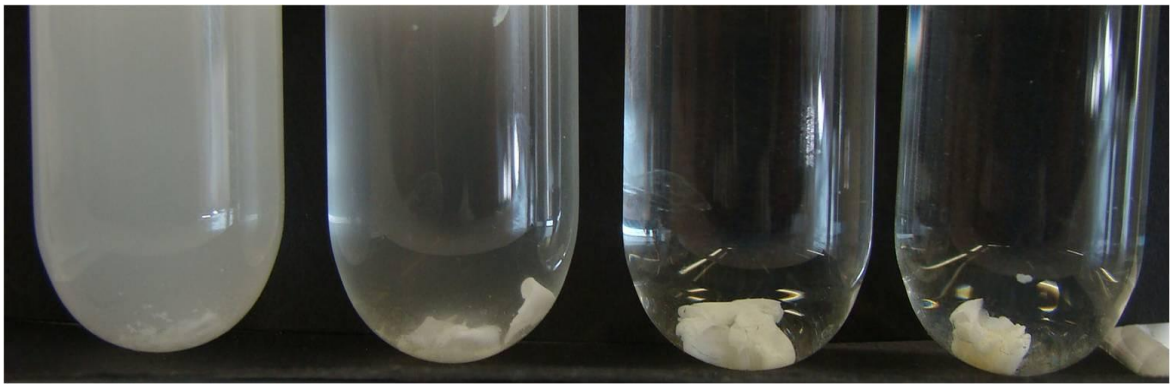


Fig.I.6 : Immersion in water of laboratory reproductions of white paint made with *Vulcano V7* and *Cenógrafa* white (from left to right): unaged and after 500h, 1750h and 4000h of artificially aging.

1.5. Cleaning vinyl paints: preliminary results

Informed choices for cleaning methods and products that can be safely used in the treatment of contemporary paintings benefit from the information gathered through the characterization studies of paints and materials and the subsequent degradation studies. Similarly to what happened in the treatment of *Inadequate Readings* (Appendix VI) one can use mock-ups where treatment can be tested and assessed establishing what is the less invasive method that can be used in the work of art at our care. Prior knowledge about the materials composition and the way these change with time is necessary to better rationalize the results obtained. Moreover, once it is

established that composition/molecular changes occur with aging the tailored reproductions and aged samples can be used for testing in a closer scenario that what happens to 'real' paintings. Therefore, the immersion/cleaning tests were performed on aged samples. One set of samples artificially aged and one set of naturally aged samples were chosen to be tested.

1.5.1 Artificially aged samples: materials and methods

These samples consisted of paint reproductions of a PVAc emulsion paint containing titanium dioxide (rutile form) that had been artificially aged using a xenon-arc light for 3500h the equivalent to ≈193 years in a museum environment.[5, 6] During this irradiation, the mock-ups were exposed to atmospheric particulates (i.e. dirt particles) as could be seen with the optical microscope (Fig. I.7).

Relative intensities measured in the ATR spectra suggest that DiBP or, its degradation product might be deposited at the surface. Values for the C-H stretching and bending absorbance (related to the presence of the plasticizer) relative to the C=O of the PVAc are higher in the aged sample when compared to the unaged one.(See Table I.2)

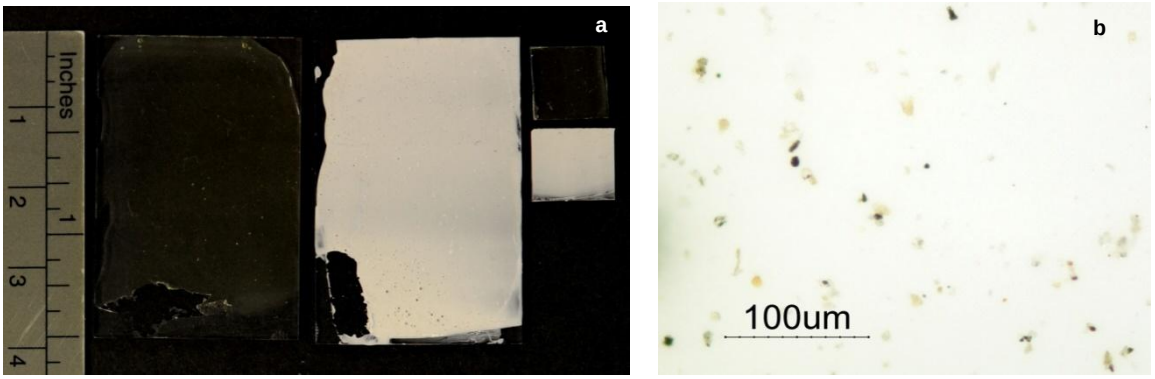


Fig. I.7: (a) artificially aged samples used in immersion tests under normal view and (b) under the microscope (obj. 10x)

The cleaning methods to be tested were selected among the most commonly used by conservators of contemporary art. For the artificially aged sample water, water and a non-ionic surfactant (*Brij700S*), and white-spirit were tested. Use of a soft eraser (*Akapad White*[30]) was also examined as this method is know to have been used in at least one of Sarmento's paintings. White-spirit was included since aliphatic mineral spirits are known to have a minimal effect on acrylic paints as has been described in the introduction. In order to ensure reproducibility and accuracy in the cleaning operation, mock-ups were immersed in the cleaning solution and tests were run in duplicate. As previous reports show that most of the material lixiviated from a paint sample occurs in the first few minutes [131, 134] the effects of five minutes of immersion were evaluated.

[30] This is a styrene butadiene rubber with several additives like vulcanized castor oil and an antioxidant, sold by *Akachemie Deffner & Johann* (Germany).[140]

1.5.1.1. Color changes

All artificially aged samples became whiter after immersion or cleaning as can be seen in the increase of the L* values; and became less yellow as can be seen in the decrease of the b* values. Differences are not significantly visible except for the sample immersed in water + *Brij700S* with a ΔE =2.23 showing the increased efficacy of an aqueous solution containing a surfactant.(Table I.1)

Table I.1 – Colorimetry values taken on artificially aged samples before and after immersion and cleaning tests. The values presented are the average of three measures in each sample.

	Before cleaning			**After cleaning**		
	L*	**a***	**b***	**L***	**a***	**b***
Water	90.41	-1.26	3.77	90.60	-1.05	2.53
	±1.30	±0.11	±0.58	±1.09	±0.25	±0.21
			ΔL*, Δa*,Δb*	0.18	0.21	-1.25
			ΔE		**1.28**	
White-spirit	90.61	-1.50	3.99	91.23	-1.11	2.55
	±0.31	±0.02	±0.11	±0.44	±0.03	±0.14
			ΔL*, Δa*,Δb*	0.61	0.39	-1.43
			ΔE		**1.61**	
Water + surfactant	93.65	-1.28	5.80	94.37	-0.80	3.75
	±1.12	±0.07	±0.73	±0.78	±0.05	±0.41
			ΔL*, Δa*,Δb*	0.72	0.48	-2.05
			ΔE		**2.23**	
Eraser	90.95	-1.39	4.76	91.42	-1.08	2.06
	±3.51	±0.07	±1.87	±3.64	±0,25	±0.05
			ΔL*, Δa*,Δb*	0.47	0.31	-0.99
			ΔE		**1.14**	

1.5.1.2. FTIR-ATR

What seems to be loss of plasticizer was detected in all the immersed samples except for the sample immersed in water (see Table I.2) Infrared absorptions were normalized for the C=O stretching in the unaged, aged control sample and immersed/cleaned samples. The decrease of absorbance of the CH stretching from the methyl (≈2970cm^{-1}) and methylene groups (≈2930cm^{-1}); the bending of the methylene groups (≈1430cm^{-1}), and CO stretching (≈1243cm^{-1}) and C-C stretching (≈1070cm^{-1}) approximates the ratios to the ones obtained in the unaged sample. Although in most samples variations are ≥9% there seems to be a trend in all the immersed and cleaned samples. The values seem to indicate that with aging in these samples with aging there was migration and deposition of additives on the paint's surface and that solvents and other cleaning products might remove it, even aliphatic ones like white spirit.

Some infrared spectra showed residues particularly in the sample immersed in water plus Brij 700S (Fig. I.8) and in the sample cleaned with the *Akapad*. Regarding residues of detergent that means that clearance of the sample after immersion was not complete. Regarding the rubber, comparative research conducted on several dry cleaning methods has shown that *Akapad* white can be used successfully as a dry cleaning method as long as the surface is cleaned thoroughly with a brush (at least three times) to remove particulate residues.[140] Despite that sponge crumbs were cleaned with a soft brush, residues remain in the surface as can be seen in the ATR spectra (See Appendix VIII) and on the AFM analyzes (Table I.3). This was somewhat expected because mechanical action is needed for the sponge to work and these vinyl paints are soft at room temperature incorporating easily any substance that comes into contact with the surface.

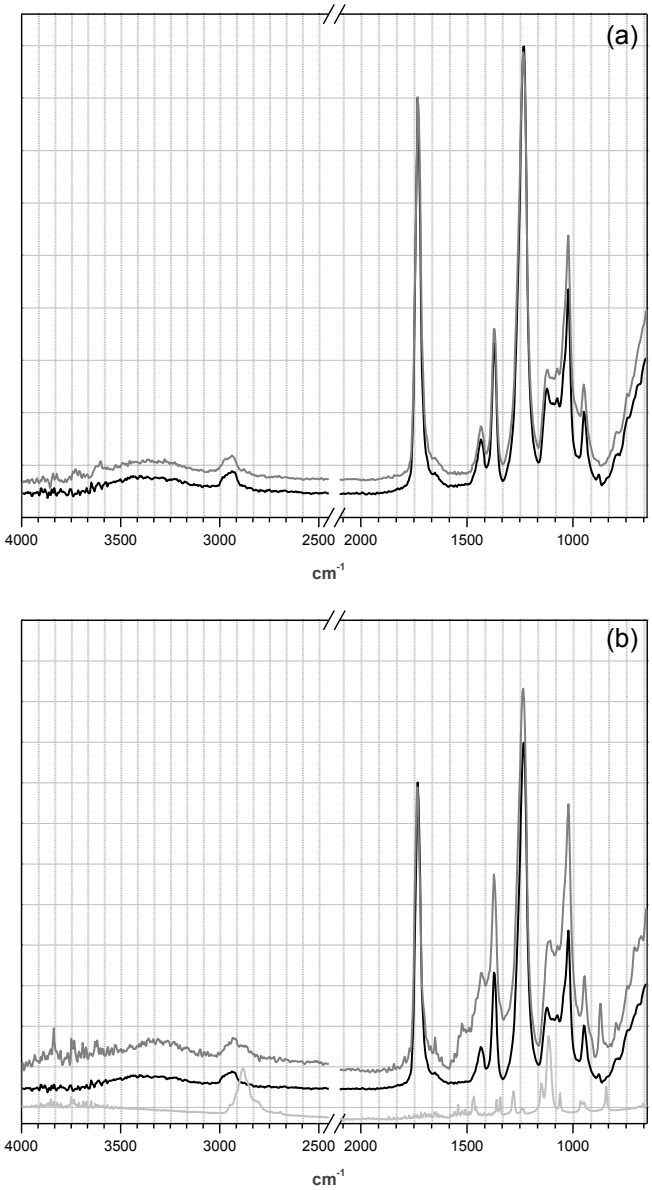


Fig. I.8: ATR spectra of the paint's surface (a) control sample (—) and after immersion in water (—); (b) control sample (—) and after immersion in water + *Brij700S* (—) and *Brij700S* (—).

Table I.2: Infrared absorptions (from ATR spectra) normalized for the C=O stretching for the vinyl titanium dioxide white paint used in immersion tests.

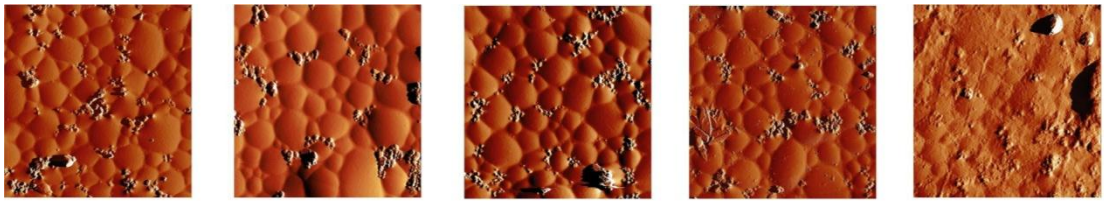
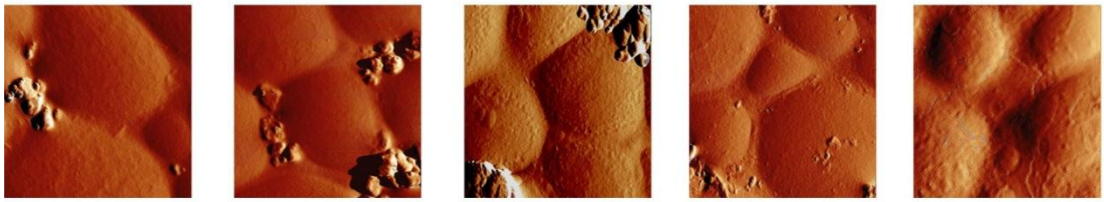
	νC-H	νC-H	νC-H	νC=O	δC-H (CH_2)	δC-H(CH_3)	νC-O (CO)O	νC-C	νC-C	ν C-O O(CH)	νC-C
Control Sample unaged	**2961-51**	**2933-31**	**2888-74**	**1736-31**	**1436-30**	**1373**	**1234**	**1124-21**	**1073**	**1022**	**945**
	0.06 ±0.01	0.07 ±0.01	0,03 ±0.00	1.00	0.13 ±0.01	0.41 ± 0.00	1.29 ±0.00	0.35 ±0.01	0.33 ±0.01	0.60 ±0.01	0.25 ±0.01
Control Sample artificially aged	***2984-73***	***2940-33***	***2899-48***	***1733-31***	***1436-33***	***1373-71***	***1234-33***	***1124-21***	***1076-73***	***1022***	***949-47***
	0.12 ±0.01	*0.13 ±0.01*	*0,10 ±0.00*	*1.00*	*0.22 ±0.01*	*0.44 ± 0.00*	*1.13 ±0.00*	*0.32 ±0.01*	*0.31 ±0.01*	*0.57 ±0.01*	*0.27 ±0.01*
Immersion in water	**2973-54**	**2942-33**	—	**1733-31**	**1436-30**	**1373-70**	**1234-32**	**1124-21**	**1076-72**	**1022**	**951-45**
	0.12 ±0.01	0.12 ±0.01	—	1.00	0.18 ±0.01	0.42 ± 0.00	1.13 ±0.00	0.30 ±0.01	0.29 ±0.01	0.55 ±0.01	0.26 ±0.01
Immersion in water + Brij 700S	***2965-56***	***2931-25***	—	***1734***	***1433***	***1373***	***1234-32***	***1124-21***	***1073***	***1022***	***951-45***
	0.10 ± 0.01	—	—	*1.00*	*0.14 ±0.02*	*0.41 ± 0.01*	*1.22 ±0.12*	*0.32 ±0.03*	*0.28 ±0.02*	*0.57 ±0.05*	*0.25 ±0.02*
Immersion in white spirit	**2970-62**	**2940-30**	—	**1734**	**1433**	**1373**	**1234-33**	**1124-18**	**1076-73**	**1022**	**945**
	0.06 ±0.00	0.07 ± 0.00	—	1.00	—	0.42 ± 0.03	1.22 ±0.06	0.30 ±0.02	0.27 ±0.02	0.58 ±0.04	0.25 ±0.02
Cleaned with Akapad	***2965-56***	***2931-25***	—	***1734***	***1433***	***1373***	***1234-32***	***1124-21***	***1073***	***1022***	***951-45***
	0.08 ±0.01	*0.10 ±0.01*	—	*1.00*	*0.16 ±0.00*	*0.41 ± 0.01*	*1.16 ±0.05*	*0.30 ±0.02*	*0.27 ±0.02*	*0.56 ±0.03*	*0.24 ±0.01*

(—) the value is not presented because the error value for this relative absorbance was too high.

1.5.1.3. AFM

For the artificially aged samples it was observed that when immersed in water, the surface displays no relevant alterations; when comparing with the immersion on water plus surfactant it is possible to observe that the smoothness of the latex particles is lost, and the polymer surface displays a more irregular texture; white-spirit cleaning promoted the appearance of holes and large protruding features on the polymer surface; with the eraser, the texture changed due to the deposition of eraser or eraser additives in a pattern similar to that observed when using the eraser directly on mica sheets; and, in some areas the surface looks flatter, presumably as a consequence of physical abrasion and flattening due to mechanical force.(Table I.3) As general conclusions, with the exception of the cleaning by eraser, the surface roughness was not significantly affected. The more relevant changes in the paint film morphology were observed with the eraser and water with surfactant.

Table I.3. AFM amplitude images of white paints artificially aged (3250h Xenon irradiation), before and after a cleaning treatment. Roughness is calculated for 10x10µm scan areas.

	Control sample	Water	Water+Brij700S	White-spirit	Eraser
10x10µm					
2x2µm					
Ra[#](nm)					
	21.0 ± 3.7	21.9 ± 4.2	23.5 ± 5.6	21.2 ± 4.3	12.4 ± 1.8

[#] Two different mock-ups were used for each cleaning product, with the exception of the white spirit sample; Ra was calculated as the average value for the two samples, and for each two different scan areas were analyzed. For each of these scan areas Ra was calculated as an average of five selected 2x2µm areas.

1.5.2. Naturally aged sample: materials and methods

A naturally aged sample was obtained from the canvas leftover that had been donated by the artist for research purposes (Fig. I.9.a). After the application of the white paint a canvas was stretched and too much fabric was left on the back. This excess canvas was cut off and was kept around the studio since the beginning of the 90's. The white paint is a PVAc emulsion with dibutyl phthalate

mixed with white pigment lithopone and calcium carbonate as a filler. The surface has a yellowish tone and was covered with a heterogeneous layer of dirt (as observed in an optical microscope and cross-sections, Fig. I.9.c and Fig. I.10). Micro-samples of dark, brownish and yellowish particles scattered on the surface were analyzed by µ-FTIR revealing the presence of organic (e.g. hydrocarbons) and inorganic substances (e.g. calcium carbonate, pigments, siliceous particles). As a clear indication that the dirt has become embedded in the paint's surface there was some difficulty in obtaining an efficient separation of the dirt from the paint; therefore PVAc was detected in the most of the dirt particles samples.

For the naturally aged sample cleaning simulation was using cotton swabs moistened in distilled water. Application times of one minute were chosen as preliminary tests made with saliva and distilled water showed that this would be sufficient to remove the layer of dirt from the surface.

The effects of cleaning (both efficacy of dirt removal and changes to the paint film) were assessed by following the level of dirt removal, color change, loss of extractable material, detection of residues; and, disruption of the paint's surface. Changes of surface morphology were monitored with AFM in the tapping mode in areas of 50 µm, 10µm and 2µm; alterations in the surface's chemical composition were assessed by FTIR-ATR; and colour coordinates were measured with the CIE-Lab* system.

Fig. I.9: Detail of the painting leftover kept at Sarmento's studio since the beginning of the 90's. The paint's surface under the stereomicroscope (b) recently painted surface (mock-up done by Sarmento) and (c) the dirty surface of the painting leftover (both with obj. 3.2x).

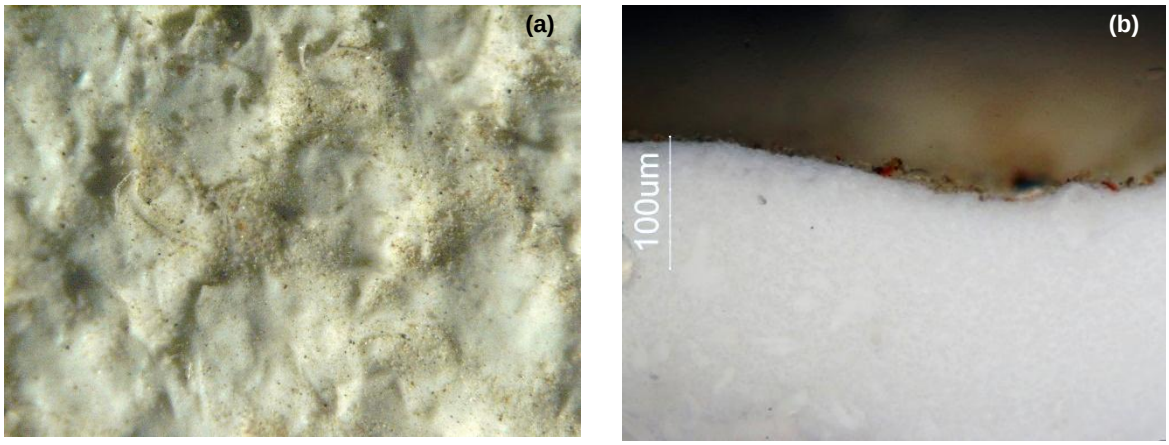


Fig.I.10: (a) The paint's leftover dirty surface under the stereomicroscope (Obj. 7.5x). (b) cross-section of the paint under the optical microscope (reflected polarized light; magnification 20x).

1.5.2.1 Color changes

After cleaning half of the surface with a water moistened cotton swab there was a significant change in the color. The diference in colour between the soiled and the cleaned paint surface is clearly visible (Fig. I.11) with a naked eye and a value of ΔE =10,59 was measured. The sample become lighter (the L* value increased) and less yellow (b* values decreased). (Table. I.4)

Fig. I. 11: Detail of the naturally aged sample, left side the untouched dirty surface; right side cleaned with a distilled water moistened cotton swab.

Table I.4 – Colorimetry values taken from the naturally aged sample after cleaning performed with water. The values presented are the average of three measures in each area.

Dirty area			Cleaned area		
L*	**a***	**b***	**L***	**a***	**b***
83,16	2,13	14,40	**90,67**	-0,14	7,30
±0,13	±0,07	±0,16	**±0,13**	±0,02	±0,03
			ΔL*: -7,51	Δa*: 2,27	Δb*: 7,11
				ΔE: 10,59	

1.5.2.2. FTIR-ATR

The ATR infrared spectra (Fig. I.12) showed that dirt was efficiently removed from the surface. The spectrum of the soiled surface is similar to the spectra of the analyzed dirt particles. Water left a clear vinyl lithopone white paint. In both cases surface analyzes and microsamples taken from the bulk of the film do not show visually significant molecular differences.

The error found in the calculation of the relative intensities and areas of absorbance bands was too high to take these values in consideration. More samples would have to be tested so that reliable conclusions could be made. However, shifts in the absorbance of the CH stretching suggest the extraction of the phthalates by the water. The initial value of the vCH from CH_3 and CH_2 respectively at 2965-58$cm^{-1}$and of 2936-31cm^{-1} shifts to 2977-60$cm^{-1}$and of 2930cm^{-1} which are values close to a PVAc free of additives.

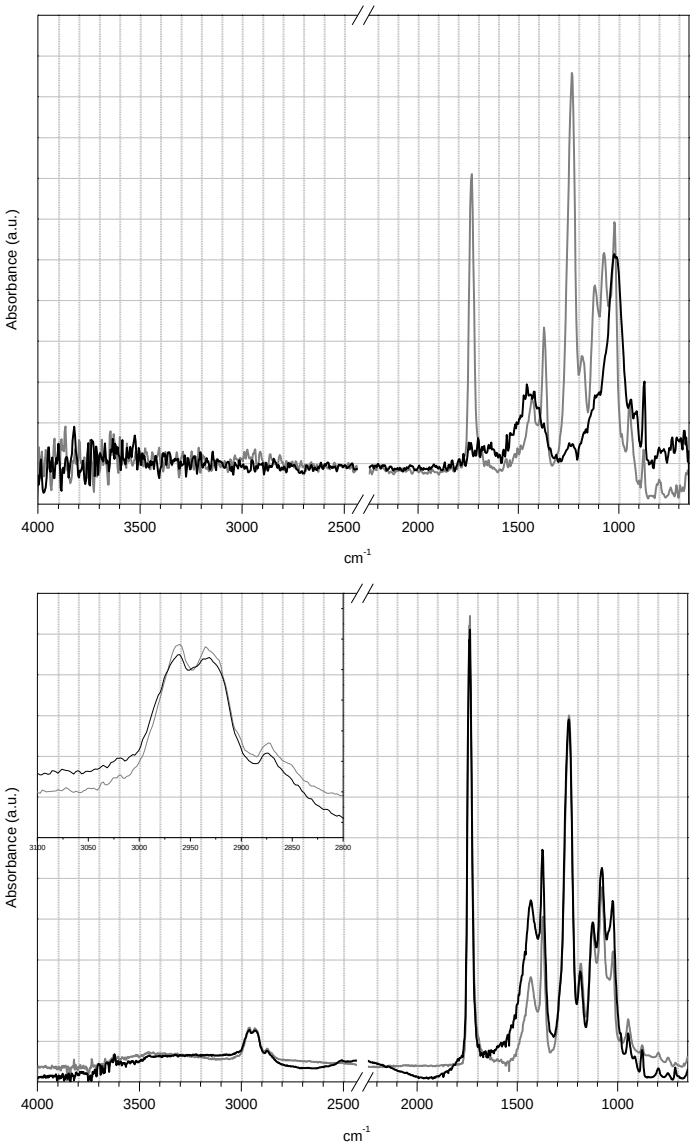


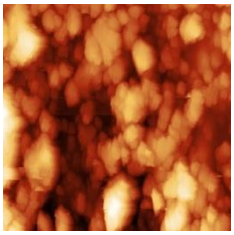
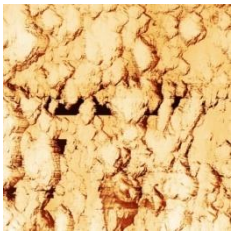
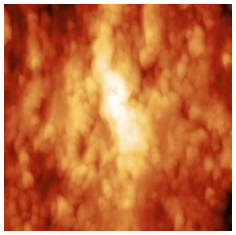
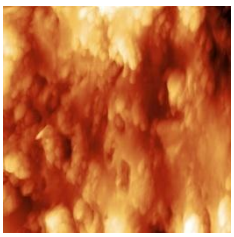
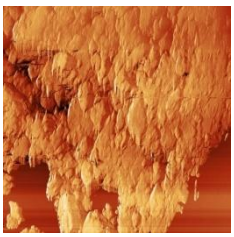
Fig I.12: (a) ATR spectra of the naturally aged sample before cleaning (—) and after cleaning with water(—). (b) Spectrum (diamond cell) of the same sample before cleaning (—) and after cleaning with water(—).

1.5.2.3 AFM

For the naturally aged paint after cleaning with water a significant reduction of the surface roughness was measured and the surface seems slightly more regular visually.(Table I.5) The reduction of rougness could be due to the removal of dirt but, also to the mechanical action of the cotton swab used to clean the surface.

On this sample other characterization values of the surface were obtained namely the pH and conductivity before and after cleaning.(Table I.6) Distilled water does not seem to have affected the paint as both values are almost equal. Regarding conductivity there is a significant decrease in the value. This decrease should be related mainly to the dirt removal. However besides the deposited dirt, pigments and binders, other paint components (e.g. additives) all contribute to the overall ionic strength of the paint surface. Therefore, further tests should be conducted in order to evaluate if any of the paint components was removed. (See Appendix VIII, Cleaning synthetic paints for further discussion of the meaning of theses values).

Table I.5. AFM height and phase images of the white paint naturally aged, before and after cleaning with distilled water. Roughness is calculated for 10x10µm scan areas.

	Dirty sample		**Cleaned with water**	
50x50µm				
10x10µm				
	Ra[#](nm)			
	489 ± 141		149 ± 25	

[#] Only one sample and one cleaning product were tested. Three different areas were imaged in the soiled and in the cleaned part of the sample. Ra was calculated as the average value of five selected 2x2µm areas.

Table I. 6. pH values and conductivity measured from the surface of the soiled and cleaned naturally aged paint.

	pH	**Conductivity (µS/cm)**
Soiled paint surface	6,7 ± 0,1	320 ± 43
Cleaned paint surface	6,6 ± 0,1	28 ± 3,6

1.6. Conclusions

Common solvents and products used to clean contemporary paintings may have a detrimental effects on the paintings. Some may have negligible consequences however others may have a higher detrimental effect. Regarding the preliminary cleaning results care should be taken when conservation treatments are considered. Ethanol and water should be used carefully as some evidences point to the removal/diffusion of additives from the paint. Besides the ethical question of treating a painting with the least interference on the original materials and properties there is also the question of the long term effect of the induced alterations. Further testing assessing the effects of the removal of paint components from vinyl paints using solvents is therefore needed (e.g. on the mechanical properties and visual characteristics of the surface).

Long exposure to water seems to solubilize some of the additives, namely poly(vinyl alcohol); longer exposure to ethanol dissolutes the polymer itself and the plasticizer. In both cases the surface may be disrupted The use of cotton swabs may affect the topography of the paint's surface. Unsurprisingly rubbers/sponges should be used followed by the proper and extensive clearance of residues on works made with vinyl paints. The same can be said when detergents are added to aqueous solutions.

Despite the questions raised by the effects of cleaning solvents on the vinyl paints Sarmento's works raise a very important ethical question. Especially in the works done in the 90's Julião explanined that a dirty water (that is water with some soil or, dirt mixed in it) would be spattered across the surface. That will leave a conservation problem to solve as a distinction will have to be made between what is 'dirt' that belongs to the surface of the painting and dirt that has naturally deposited on the surface due to exposure to the ambient environment.

Conclusions and further work

Julião Sarmento's painting materials and works are a clear example of how complex research in contemporary paintings can be. Different approaches had to be set and interweaved: the informations gathered near the artist, the characterization of the materials used, the methods used to manipulate those materials, the creation of accurate laboratory reproductions, the aging conditions and the rationalization of the observed behavior with aging. Either if the purpose was its characterization, understanding the observed degradation problems or, the expected (or, unexpected) reaction to treatments the most comprehensive characterization of the materials present was sought and was only achived by using a multi-analytical approach.

Artificial aging showed that the most recent formulations which are based on a poly(vinyl acetate), poly(vinyl chloride) and polyethylene terpolymer are less stable when compared to some homopolymer formulations. These results raise awareness that further testing should be made in the modern colored *Sabu*s because these paints continued to be used by artists until its production cessed not so long ago.

From the four pigments studied, titanium dioxide rutile and a carbon based black proved to be stabilizers for both types of polymer in almost all the paint's characteristics studied. The mixture lithopone plus calcium carbonate has showed to have a photocatalytic effect on the binders: it increased chain scission, cross-linking, surface roughness and yellowing either when used with the homopolymer or, the terpolymer.

Natural aging showed the sensitizing effect of *Cenógrafa* white (lithopone+calcium carbonate) on the homopolymer regarding yellowing. The discoloration observed in samples containing the hompolymer and this pigment is close to the discoloration observed in the studied paintings. Although it was not possible to establish the exact chemical process involved there seems to be some evidence that suggests that double conjugated bonds might be being formed in the polymer. If one considers the absorbance in the near UV of this pigment is actually used for UV curing of polymers one should expect it to influence the polymer's photodegradation. The current works created by Sarmento are expected to be more stable as they were painted using the rutile titanium dioxide. In both aging regimes this pigment showed to have a protective role on the binder.

As was seen in the naturally aged samples discoloration of this white paint seems to be irreversible and ongoing and is still a major concern.

As expected loss of plasticizer was found to happen from the homopolymer emulsion. However further analysis also disclosure that it is degradating. It might be significant that the emulsion containing DiBP instead of DBP (which did not show signs of being degraded) showed an increased tendency towards yellowing when exposed to natural light.

The studied paintings showed to be in an overall good state of conservation except for the paintings created in the 90's with white glue and white lithopone. The disapearance of the plasticizer was the only change detected by infrared in accordance to what happened in the laboratory aged samples. Yellowing of the pure Vulcano *V7* seen in artificial aging correlates well

with what is observed in Sarmento's paintings. Areas that are very rich in binder with almost no pigment show this discoloration.

Immersion/cleaning tests showed that artificially or, naturally aged vinyl based paints can be susceptible to organic solvents like ethanol and water as some evidences point to the removal/diffusion of additives from the paint. The observations made point to the need to proceed further in this research field.

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Appendix Ia: Interviews with Julião Sarmento (translated to English)

1.1. Interview 1: 12th of January of 2004

Participants Julião Sarmento and Ana Isabel Pereira

At the artist's studio (Centro Empresarial de Sintra-Estoril, n.5, Armazén B-8)

The first interview with Julião Sarmento was conducted in 2004 during a Project for the masters degree in Conservation and Restoration. [19] The core of the project was the study of the painting *Just a Skin Affair* from 1988. In addition to acquiring information regarding this particular work there was a holistic approach. Questions were made regarding Sarmento's description and opinion of his materials and techniques and his view on the preservation of his work. The information gathered at that time was invaluable for the research conducted afterwards. Hence it was considered essential to include it here.

Introduction

Ana Isabel Pereira: In an interview to Germano Celant [88] Sarmento states that "…a painting is simply a tool to express some ideas…because, at the end the objects produced by me, although they are made of a canvas and have the traditional look of a painting are not exactly paintings, at least for me they are not." What exactly do you mean with this statement?

Julião Sarmento: You need to put things into context…the context of that question is the concept of the work in itself, of its creation. The fact is that those are not paintings because the painting in itself is not what interests me…what I seek when I make a painting is not the painting in itself, the painting is not an end, it is just a means to get somewhere. While traditional painters like Kieffer or Baselitz or the new German Expressionists, or some English painters like Per Kirkeby or, Paula Rego…painting for them is a means and an end. Therefore, the means to that end is painting. For me, painting is just a means to an end, what interests me is not the painting. It is what is underneath the painting. Let's say we have two types of school, and Baselitz represents one of the schools, I identify myself with the school represented by Polke, which uses painting as a means not an end, he is not a painter like Baselitz is. Polke uses painting as a strategy. That is what I do…strategy not in the sense of a tactic but, as a means.

AIP: When we make a review of your works we find a vast exploration and combination of materials and techniques: canvas (stretched and loose), paper; wood, plastic, photography, metal, acrylic glass, cork platex, earth, graphite, cardboard, gravel, acrylic and so on. Do the materials you use have a role beside form and colour?

JS: Yes, they do…Do you mean if they have a certain importance? Yes, they have a certain weight…

AIP: David Smith (1906-1965, EUA) made the following statement in 1959 "Genuine oil painting was some highly cultivated act that came like the silver spoon, born from years of slow method, applied drawing, watercoloring, designing, art structure, requiring special equipment of an almost secret nature…and when I got to New York and Paris I found that painting was made with anything

at hand, building board, raw canvas, self-primed canvas, with or, without brushes, on the easel, on the floor, on the wall, no rules, no secret equipment, no anything, except the conviction of the artist, his challenge to the world and his own identity.". What comments would you do on this affirmation? [141]

JS: The only comment I could make is that I totally agree.

AIP: On this painting [*Just a Skin Affair*, 1988] and on most of the paintings belonging at the CAM-FCG you can see that every canvas has colours, brushstrokes and surfaces that are very different in terms of texture and gloss. Every element is painted in a different form. You can either find larger and schematic brushstrokes, while others are thinner and more regular. Some surfaces are uniform and smooth while others are rougher and irregular. This working method reminds me of Maria de Corral's statement about painting in the 80's "…the need of figure and image, of the pictorial gesture…for the pleasure of painting, the taste for the pigment and for the materials". [88] In your opinion is there such a relation in these paintings?

JS: Yes and no, you are talking about three paintings that are from a completely different period. *Noites Brancas* that I think is from 81 or, 82; *Just a Skin Affair* from 1988 and *An Involved Story* from 98…and *Frozen Leopard* from 93. That statement could be related to the painting *Noites Brancas* which is from 1981, because at that time I had an experimentalist approach regarding the materials. It is like the statement from David Smith. On one hand I had an experimental attitude with the materials, and I would really enjoy trying new materials. On the other hand, I would also use everything that I would find at hand, that would be easy to attain, that was cheap. At that time I did not have the financial means I have today. I would take advantage of that as a strategy and use poorer and cheaper materials.

In other words…for reasons that have nothing to do with artistic intent I was forced to use those poorer and cheaper materials, because I had no other choice. However, that would not stop me from doing what I wanted to do. Therefore, I adapted what I wanted to do, to the chances I had of acquiring a certain type of material and got accustomed to working with common materials. I was a never an artist (and even today when I could do it) that would use expensive materials and the best brushes. I have no fun with those. I want to work transforming things that are worthless into things that start to be valuable. I think that's it. But at that time I was coming from a very complicated period, from the 70's to the beginning of the 80's…well especially from the 70's, from a very theoretical base, of a consistent work…a phase of conceptual works that end up being so predictable that they irritated me. That corresponded to the time I begin to paint again at the beginning of the 80's. Therefore there was very much the sense of the exercise of freedom. That drove me to experimenting with things, to use what I had at hand. Although I would walk two meters if I wanted to use something in particular. Nevertheless, I would not move if it was possible …and then I would adapt what I wanted to do to with what I had at hand.

Materials and techniques

Paints

AIP: Although my observation is focussed on the four paintings owed by CAM-FCG I would like to talk to you about the paints you have used and still use.

JS I have used a huge variety of paints. The type of paint least used was oil. I made around three or, four paintings with it. Since, oil takes a long time to dry and I'm too immediate, I do not have the patience and…in fact we had a dogma, we were 20th century artists and oil?!...Then I got used to working with other types of materials. At the beginning of the 70's I worked mainly with acrylics. Then I worked…(I'm sort of doing a summary without many details)…when I stopped painting around 1974 I started working with photography, text, film, video and sound and so on…with reproducible materials let's say. When I started painting again I started to use acrylic tempera, I worked with *Sabu* paints from Casa Varela. And then I started using pigments with PVAc, I started making my own paints, mixing dry pigments with PVAc. The pigments could be industrial that you buy in a store or, pigments I made myself, with garbage. I would sweep the floor and that was pigment.

AIP: You mentioned in an interview with Germano Celant that you made your own pigment so that you could create different types of surface and, in fact the analysis conducted so far on the work *Just a Skin Affair* reveals that some of the paints were made by you. Also on the four CAM paintings the manipulation of the paints to give different visual effects is evident. In the same painting I can find matte and shiny surfaces; or smoother and irregular surfaces. The question is how can you get these different effects? In other words how do you manipulate the paint characteristics?

JS: That depends on a number of things. From the PVAc quality which is not always the same, to its consistency after diluting in water (sometimes I use more water, other times I use less), I mix the pigments very well or, not at all. It is a complicated technique…and it is not…it's relatively easy to achieve but, it has several steps. For example, if you have a portion of PVAc and a portion of titanium white you have numerous ways to obtain a different surface appearance after drying, it can be shiny, it can become very matt, it can be very smooth or, very irregular. It depends on the amount of water you add, it depends on the way it is mixed (if you mix it unevenly or thoroughly). Using the same amount of pigment and binder you can get a very different result. Then if you vary the ratios the possibilities are endless.

AIP: So, the only things you use to make your paints are the binder and the pigment…

JS: Generally speaking I use binder, pigment and water. But, that does not mean that once in a while I won't use something else. I'm very free at work and I do not have dogmas. If suddenly I feel like doing something else I will do it. My paintings are not all equal in terms of technique; eventually you can find a painting where I used something else. Let's just say that there is a general trend that I use in 90% of my work and that is the technique I just described.

AIP: What are the practical and aesthetic properties that this binding medium offers and that you could not attain with other binders?

JS: Comparing to oil it's the drying speed, the kind of surface that I could not achieve with it and the price. Imagine what it would be like to paint a six square meter surface with oil with that kind of substance. It would take months, years to dry it would probably cost a fortune and I would not get the kind of surface I want.

AIP: And comparing with the acrylics?

JS: You are talking about normal acrylic paint tubes? I simply do not use them. I just use acrylics when I want to do something very specific, relatively small and with weird colours that I cannot find in the range of the dry pigments I buy.
AIP: You mentioned that you use different qualities of PVAc so, I can assume you do not always use the same paint.
JS: No, I usually use PVAc from Casa Varela. They sell it in big plastic containers…
AIP: Was it easy to find information regarding the practical properties and durability of these products?
JS: I never worried about it.
AIP: Do you know international or Portuguese artists that use the same paints and methods that you do, mixing yourself the binder and the pigment?
JS: I know that Barcelló used it and I don't know if he still does. José Maria Sicilio used it but I don't know if he still does...I don't mean to say there are not more…probably there are, but I don't know them.
AIP: How do you usually apply the paints to make the background of the paintings?
JS: It depends sometimes with brushes, sometimes with spalter brushes, sometimes with my hands, sometimes with paint rollers, sometimes with wooden sticks. It depends on the background…sometimes I just let it flow.
AIP: You usually have the canvas lying in the floor?
JS: Yes, almost always the canvas is on the floor. I just spread the canvas on the floor and do the work there.
AIP: On some of your paintings the background colour is done with overlaid paint layers, some of which do not show at the surface. For example, in *Just a Skin Affair* you can find four paint layers that cover all the canvas and two partial ones. Do you usually work overlying layers?
JS: It is possible yes…I did that painting a while ago. At that time I would work like that but, nowadays I don't anymore. On the *White Painting* series I do not work like that. Sometimes I use two, three layers at the most but, generally I only use one paint layer.
AIP: However, on the White Paintings series there is a difference of gloss in large areas of white paint…
JS: Yes. But, that difference in the surface is a consequence of the technique I explained. Because of the way the binder, pigment and water are mixed.
AIP: Why would you paint with several layers?
JS: For many different reasons. Because I did not like the colour and I wanted to change it. Because I thought the best way to reach a certain colour would be to use transparency. Because I would achieve more or less random areas of different colour. These would all be different reasons and in this case I'm not sure. I do not remember anymore. There could be a fourth reason. At that time I would work simultaneously in several paintings and I would do, for example a yellow background which I could leave lying on the floor for several months. Meanwhile I did not wish to continue with the project in the yellow background. Then I would get a new idea for another

painting but, I would not need yellow I would need red. I would cover the yellow with red paint. So, sometimes it could be a question of recycling the canvas.

AIP: Was that a slow job having to wait for the paint to dry before applying more paint on top?

JS: In some cases yes, for example in the case I just described. On other cases, for example for objective reasons it would be slow but, not so slow. As you know this dries very fast. Sometimes I would not want the paint to dry so fast so I would apply several paint layers to which I added plenty of water, so they would also be transparent. It was the case of *The Swiftness of Skin* and *Boys Town*[31] among others.

AIP: The colours used in your paintings seem to be restricted to a narrow range of colours, earths, greys, yellows, greens and reds. Later they are even more restricted to white, black and grey. There is definitely a preference for certain colours, right?

JS: And there is. Except for the work done in the beginning of the 80's where there is a very short period in which I used vibrant reds and greens. After that my colour palette got narrower merely because I chose it to be like that. Those colours did not interest me. I think they are distracting me from the essential. You start looking at the yellows, pinks and so on which may be important for some people but, not for me. And these days I practically just work with black and white.

AIP: What kind of pigments do you use?

JS: Generally I use dry pigment. Sometimes I use concentrated liquid pigments from Winsor&Newton and from Talens, because the colour I want does not exist in dry pigment or, because I'm looking for a more intense colour. But, those pigments always go with another colour. I never mix them only with the PVAc. I first do a white paint and then I tone this paint with those pigments. If I mix those pigments directly with the PVAc, the colour will not hold. What happens is that as it dries you get this transparent greenish or reddish stuff.

AIP: Then I can assume the dry pigments are sold in a very limited colour range when compared to coloured paints?

JS: Of course they are.

AIP: And you do not feel that can end up limiting your work?

JS: No, for two reasons. Because as I explained I use by choice a very restricted palette of colours and the dry pigments that I buy match my purpose. When I want something that does not exist or, I want to change the colour a certain way I use the other ones I mentioned. This does not mean that I only use pure dry pigment as I buy it. If I want to change the colour I will change it.

AIP: The results of the analysis done on *Just a Skin Affair* show that some paint layers have a very restricted number of pigments mixed together and others have a larger number of pigments. However in the latter it seems that this is due to paint contamination. For example, when preparing these paints you might have used a recipient that had traces of other paints. Do you do this often? Use the same recipient to do the paints?

[31] *The Swiftness of Skin* belongs to a private collection but, is kept at the Fundação de Serralves - Museu de Arte Contemporânea in Oporto. (http://www.serralves.pt/pt/museu/a-colecao/obras-e-artistas/?l=S#tabs2_5-html) *Boys Town* is property of the Hara Museum of Contemporary Art in Tokyo. Both paintings were painted in 1989 and are catalogued as acrylic paint on canvas. (http://www.haramuseum.or.jp/en/common/collection/clc_dtl.php?AstID=244)

JS: It would depend. If I wanted to do a painting more thoughtless like this one then I would not bother. However if I wanted to do something pristine for example, if I want the painting to be really white evidently I would not work like that. It's common sense. The colours you see in this painting, more than colours, are murky colours that were attained with the leftovers of other paints. Sometimes (I am not sure if this is the case) I would be working on seven or, eight paintings at the same time. As I work with plastic buckets if I needed some paint I would grab the remains and put them all together whatever the outcome would be. The colour would be random.

AIP: The surfaces of your paintings are very textured and irregular, they are full of material. And that is not only achieved with the paints and the way they are applied but, also through the addiction of granulated substances. Why and when did you start to use this textured effects?

JS: Why?! Well, that is not a technical question. Why? Because I felt like it. That started in the 80's…the surface of the canvas started to be become tangible for me, it had to be tactile and I was interested in showing the differences of the surface through it. I realized that I could alter the surface using different tricks like sand, poorly mixed pigments, tobacco. I have paintings with tobacco, matches and pieces of paper.

Materials and techniques

Supports

AIP: Although you worked with several kinds of support like paper and hardboard, canvas seems to be your support of choice from the mid 80s until now. Why this preference for the textile support?

JS: Because I have been lazy to look for another kind of support. And it is not really a canvas, it is what the British call 'Cotton Duck', it is cotton. It is incomparably cheaper and it has something that linen does not have which is it has a will of its own. Linen is much more stable. Cotton will be loose when it is wet, it can stretch or reduce and I like paintings that have a life of its own and that change. I don't like unchangeable things. I like things where we can see the passage of time. So…Its like in the *White Painting* series the PVAc turns yellow, in a few years they will be yellow. Some of them have already turned yellow. It does not change into a bright yellow but, it does get yellow. I knew that. It is not something that I found out later. That aging of things, that formal modification of things is something that interests me. Therefore, the question of using cotton also has something to do with that. The support is not stable, all of the sudden it is slack and we have to stretch it. All that constant handling of things is something that interests me on a theoretical level.

AIP: In at least two of the paintings from the CAM the canvas supports are stretched either by you, or by an assistant. Why would you choose a more traditional method and assemble the painting's structure yourself when you could buy ready to use canvas?

JS: All the works owed by the CAM were stretched by me. It was only a while ago that I had assistants doing that work. I had fun doing it. But, all of the sudden I started to get older and lazier and these days it is my assistant that does that job. But, I have stretched thousands of canvas. I'm a fanatic for it to be properly stretched. There are no industrial cotton canvas, there are not. There are only in linen and in pre-prepared linen. I work on the raw cotton. I do not use what is called

primed canvases. And there is also the problem of the thickness of the stretcher. Nowadays, I work with eight centimetre thick stretchers and that is not commercially available. I'm also a big defender of freedom on the studio. If I feel like doing a painting of 77.8cm by 99.7cm that is what I will do. I do not feel like using a size that someone tells me to use.

AIP: And having it made by size?

JS: All my canvases are made by size.

AIP: You mean the stretchers?

JS: Yes, I mean the stretchers. I decide the size I want the paintings to be. Then I order the stretchers just the size I want them to be.

AIP: Working with big paintings, that are difficult to manipulate, with the cotton reacting to the water from the emulsion binder I guess you would have the necessity to stretch them temporarily? Or, in other words, how do you manage having a free support and the cotton reacting while you paint?

JS: No, I only stretch the painting when it is completely finished…well…it depends right now I'm working a series of paintings where part of the painting is done out of the stretcher and the other part is made with the painting already stretched.

AIP: But, it is not the case of *Just a Skin Affair*…

JS: No, that painting was only stretched when it was finished.

AIP: But, there are some paint layers on canvas #1 that only stretch to the limit of the stretcher. In other words the paint layers do not go over the tacking margins. That is an indication that some layers were applied after the canvas was stretched.

JS: I see what you mean…that canvas was painted in a different manner. It was painted using a brush after it was tacked to the stretcher. And…I do not remember anymore…is it the smother piece?

AIP: No, it is the most textured one.

JS: Do you know how this was done? The cotton was very well stretched and then, placing the canvas horizontally, I painted it with a grey made of pigment and binder thoroughly mixed so that I would create a surface that resembled hot chocolate. A paint that although is dense when you pour it over the surface would spread all over. When everything was more or, less dried, with a hose I would sprinkle water so that some water drops would fall on the surface, and that would make that effect…so, this must be water with garbage…no, in this case this was done carelessly. I would take water mix it with dirt from the studio…I would sweep the studio…and that would have lots of earth, I would mix it with the water. The water would turn brown with all that dust. Then I would wet my hand and splatter the water into the paint surface. Therefore this was done with the canvas standing horizontally.

AIP: Anyway, the paintings are always loose when you paint them?

JS: Yes, but there are exceptions. Now I had to make an effort to remember how this one was made.

AIP: Some authors see your construction of the image by joining different painted canvas as a way of showing that your speech is made of 'fragments of reality' sometimes with no apparent relationship. Do you agree with this interpretation?

JS: Yes and no. They do not have to be necessarily fragments of reality. Yes, it is an underlining of the fragmentation but, on the other hand, that fragmentation does not have to be of reality. So, I agree to a certain extent.

Ground layer

AIP: Concerning the ground layer you have already mentioned that you do not usually apply any and you do not use pre-prepared canvases.

JS: It is not a question of usually not using those. I believe that I have never used pre-prepared canvas.

Sizing

AIP: Do you usually apply a size layer e.g., an isolating layer that makes the canvas less absorbent?

JS: I also do not use that layer.

Varnishes

AIP: The surface of your paintings is very rich in visual effects because of the different characteristics and heterogonous distribution of the paint. Which suggests that you do not use a varnish as this would even the surface?

JS: No, never.

AIP: However, you have paintings where you used graphite and chalk (for example, *An Involved Story* and *Frozen Leopard*). Do you apply a fixative in those cases?

JS: Yes, I used *Elnett Satin*, which is hairspray. However, the paintings would smell a lot like a hairdresser so, I started to buy an artist's fixative from Talens or, Winsor & Newton.

AIP: Are you concerned about making a regular layer?

JS: No, I do not worry about achieving a regular layer. I only apply it over the drawing…well, it depends…if the painting is small I apply the fixative in a regular layer. If the painting is gigantic, I will not go through all that trouble and I only apply it over the drawing. As you can see I am not very orthodox when working.

AIP: Concerning all the issues we have been discussing could you describe the most relevant negative and positive experiences of the materials and techniques you use?

JS: Negative aspects? These surfaces are very tacky, the PVAc is glue and if people are not careful handling the paintings…I have had paintings practically destroyed because they go to an exhibition somewhere and then people wrap up the paintings in bubble wrap. What happens is the surface is damaged by the bubbles. That is the most negative experience. You have to be extra careful because the only thing you can put in contact with the surface is a thick polyethylene plastic. That will not glue to the surface although you cannot press it to the surface. It can also leave marks, because it can burnish the surface making it shinier.

AIP: But even if the paint surface is thoroughly dry?

JS: Yes, it will not stick to the surface like that, though with differences of temperature and of humidity...

AIP: Where do you usually buy your materials the stretchers, the canvas, the binding media, the pigments? I already know that in Casa Varela you would buy some of them.

JS: Yes, I buy most of my materials in the Casa Varela but, not always. I also go to the Casa Fernandes for some materials…I do not know…it is like going to the supermarket when people go to do their monthly shopping. Then if I need something quickly I will not go from here to Lisbon I will go to a closer place.

AIP: On the painting *Just a Skin affair* what did you use to create the brown paint layer?

JS: That is garbage. I swept the studio, when I did this painting I had a studio in Sintra in the middle of the countryside where dust and garbage would naturally go inside. I swept the studio's floor and get brown dust mixed with twigs and junk, it was garbage. Then I sifted it and I got a very fine brown powder, slightly coarser than backing powder…No, wait…that was for something else. Here I would grab all that garbage just as I would pick it from the floor and you throw it in a bucket with water and would stir it. It would look like a dirt coffee and I would throw it on top of the canvas. Therefore this must be soil.

AIP: And it retains the original appearance?

JS: Yes, just like that.

AIP: When you were talking about the garbage you were referring to the painting *Dez anos, 1986/1996*, in the exhibition *The House with the upstairs* in it in London in 1996"? [59]

JS: Exactly, during ten years I swept the studio floor and I made a pigment with those ten years of garbage.

AIP: So besides *Just a Skin Affair* and *Dez anos, 1986/1996*…

JS: At that time I frequently used garbage however not like in that one. At the time of the "Dez Anos" I made a refined pigment with that garbage. During ten years I swept the garbage…dust, not garbage but dust, because I sifted it until I got a very fine dust. And then I filled a recipient with that dust and mixed it with the PVAc as if I was making paint only the pigment was the result of ten years of dust.

AIP: Is that related to "working with what you have at hand" or, does it have a more specific meaning?

JS: In the "Dez anos" it does because it took me ten years to do that.

AIP: Why do you prefer to use lithopone white when titanium white had already replaced it and had the advantage of being more opaque?

JS: I send my assistant to Casa Varela and I use what he brings me. And that is what they put in the *Cenógrafa* pigments. If sometimes they use titanium white and other times the lithopone…

AIP: On "Just a skin affair" the disposition of the three elements was changed after making the paintings but, before they had time to be completely dry. Do you frequently change your ideas about the disposition of the various elements?

JS: The paints were already dry.

AIP: But, there are marks…

JS: I know. But, that is what I was talking about. After some years of being dried you put them together and if it is a hot day they will glue.

AIP: However, these marks on the back indicate that the canvases have been in an inverted position

JS: What happened was that I did not put these metal reinforcement elements when the Gulbenkian bought the piece the three elements were free. They putted them together the wrong way. When I saw that it was wrong I went there and they changed it. So this canvas must have been on that side. If you put these two elements together fifteen or, twenty years from now if the weather is like this nothing will happen but, if you are in August they will stick together.

AIP: Therefore you have a very clear idea of how you are going to the articulate the different elements from the start?

JS: Yes, definitely. When I am working the elements before they are stretched there might be changes. However at a certain point it is absolutely clear. When I order the stretchers everything is planned.

Important note: the union between the elements is not precise. Consequently the work is not perfectly rectangular. When a recent photo of the painting was shown Julião immediately noticed it. He was asked if that bothered him and the answer was affirmative, it bothered him.

Context

AIP: In 1968 you were in the Fine Arts paintings course in Lisbon. In an interview given to Germano Celant you refer that "I wanted to paint with acrylics, because I had seen the *Aquatec* and similar paints advertisement. And I found a store in Lisbon that had those acrylic paints. However I was not authorized to use them in school where no one had ever heard about them or, were interested in using them.".[88] How was the School of Fine Arts training in those days, regarding painting materials and techniques?

JS: After all I said you still ask that question?! It was like that, we were forbidden to use acrylic paint. In my class...let me see artists from my course that you might eventually know, at least historically, Fernando Calhau, Graça Pereira Coutinho...I do not remember anyone else, the rest went to become teachers if I am not mistaken. Anyway we were not authorized to use them. We had to use oil paints, egg temperas made by us, which is funny making your own paints. Maybe that is why I started making my own paints. It looked like a XIX century school. We had stained glass lessons...there is really no point in persisting with this issue because it was a disgrace.

AIP: At that time was it hard to find acrylic or, other synthetic paints in the stores?

JS: Yes, it was.

AIP: Where could you find it?

JS: Mostly in Corbel.

AIP: And you could only find *Aquatec*…

JS: Yes...I mean no, we could see the *Aquatec* commercial in the American magazines but, it wasn't sold. In Portugal the only ones we could find were Talens paints...I don't remember very well but I think it was from Talens.

AIP: Why did you get interested in these paints?

JS: Because these were the paints that the artists we liked were using. The American and English Pop artists of that time. They worked with these acrylic paints and they were your heroes. Those things are always done sympathetically right?

AIP: You were not worried that these were new materials with unknown characteristics and durability?

JS: No, on the contrary I liked that. We liked to work with materials we did not know.

AIP: In the same interview you refer that you did and "acrylic painting" with a friend. Do you remember the differences you found between that paint and the ones recommend to be used in the academic training?

JS: I remember we were crazy with that paint because it would dry in a second, it was plastic and would stick to things. It was joyfulness.

AIP: In 1969 you were Joaquim Rodrigo's assistant. It was the year he changed his materials and techniques. He started to use hardboard as a support and vinyl paints namely, white glue *V7*, with a restricted set of dry pigments which had a symbolic meaning.[5] Did Joaquim Rodrigo's choice of materials have any influence in your own work?

JS: I do not know. I have been asked that question and I do not know the answer. On one hand, Joaquim Rodrigo was an unbearable annoying and crazy person, completely insane. But today I see Rodrigo in a different way. At that time I wanted to get away from him. Therefore I think it is strange that I would be influenced by his methods. However, on the other hand there are facts that match. If it was a conscious or, unconscious process I do not know. For example, that interest in using little colour I think I might have inherited from him but, I cannot be sure. If I had not worked with Joaquim Rodrigo I do not know what I would be today, do you understand? I do not get on futurologists schemes. I think that it might have had some sort of influence. I do not know which but, that might have happened.

AIP: But concerning making your own paints?

JS: He did teach me that. What he taught me was that if we made the paints...he did not teach me that, I discovered it working there. Things were cheaper and that was what interested me. It was in fact a question of economy. I didn't share Rodrigo's ideas and all that craziness and there are only three colours, the red and the black and so on. But, what I saw working for him was that if I worked making my own paints it was cheaper than buying industrial paints.

Durability and Conservation

AIP: Erich Gantzert-Castrillo (conservator-restorer) from the Frankfurt Museum of Modern Art states that "Artists face many more questions regarding the durability of their materials and it is expected that they provide answers." [142] Do you accept the responsibility assigned to the artists regarding the durability of their work?

J.S: No, not at all. I am not interested. If the works disappear, they disappear. I do not care. I admit that the conservator does not want the works to disappear and that he wants to conserve them. Still that is his problem. I will put at the display for all conservators, as I have done, all the information needed. For example, the Smithsonian asked me for samples of the pigments and PVAc glue. I gave them everything, for my paintings that they have there, for them to have there,

to create a database. I will not change a millimetre of my work thinking of durability. Let's see if I have two kinds of paper that are rigorously the same and if one last one hundred years and the other lasts five than I will use the one that lasts one hundred. However, if one is slightly whiter and if I want the whiter one, I will use the whiter one.

AIP: But, for you "...artists create or, work for immortality..."...

JS: Yes, but...I think so. I think the only fundamental reason artists work is for immortality.

AIP: What is your practical experience with aging and degradation of your paintings? You mentioned the yellowing before.

JS: And that is probably the only one. And it is a calculated yellowing because I know it will happen and then it stabilizes. It yellows in a certain way and then it does not yellow any more. Curiously materials that we were told would only last a month, two months...well in the beginning of the 80's I would work with brown grocery paper which is a highly acidic paper, and the *Sabu* paints which were considered to be low quality paints. Yet the works today look like when they were made in 1980.

AIP: So, you are not concerned that pigments can lose their colour, that colour changes might occur and new chromatic contrasts appear? You are not concerned that binders might change and influence the original chromatic values?

JS: No...I mean if I can do something to prevent it from happening I will. There are some paintings that I'm working on now and I really do not want them to yellow. What I am doing is to work with acrylic gypsum which theoretically will not turn yellow. In other words I do a bottom layer with PVAc and white pigment to create the texture I want and then I paint on top with acrylic gypsum. I have a friend who is an artist - he is an American artist, one of the fathers of conceptual art - I exchanged a work with him a couple of years ago. When I received it was all messed up, it had a photograph with paint flakes. I wrote to him saying "…this is all damaged do you think I should have it retouched, that I should have it restored?". He told me that he did not want me to do that. I think this is a big lesson because you should not put makeup on works of art. It is the same as with people. People grow old and so do the works. It is like those old ladies from Hollywood, from Beverely Hills that turn into plastic, right? The works are what they are. They age as they age. They do not get worse because of that. They acquire the look of time which is also important.

AIP: Could you describe positive and negative conservation and restoration experiences of your works?

JS: Some of my works were in fact restored. However, they were always well restored. I do not remember any case were it was a negative experience.

AIP: What was the reason for their treatment?

JS: Usually it was not because of the effect of time but, because of damage caused by handling.

AIP: Do you wish to be consulted regarding the conservation state and preservation issues on your works?

JS: No.

AIP: You would like to stay outside of these issues?

JS: No. Well this is not a question of liking it or not. If at some point someone thinks it is important to get in touch with me to know some useful information in order to restore one of my works I am available. I do not mind being contacted.

Exhibition/Preservation

AIP: For you art "is a physical practice, almost physical, because I make objects that can be seen and in some cases touched".[88] From this point of view would you be in favour or against placing any of your works (either in paper, canvas or, another technique) in a glazed frame?

JS: In case of need I'm not against it since sometimes it is really important, it does protect. Those paintings on paper that I did in the end of the 80's were meant to be nailed to the wall. Yet many were vandalized. If they are inside a glazed box you can avoid that.

AIP: Although the margins are not a perfect continuation of the painting's surface your works were not meant to be framed were they?

JS: No, not at all.

Authenticity issues

AIP: Could you describe the role of your assistant in your artistic production?

JS: Essentially they help. Most often they do what I think anyone can do. Then there are those things that I think only I can do. For example, I'm doing a white background, I have a series of paintings with repeated backgrounds very similar between them, I just say "João, it is like this...". Why should I do something that is completely mechanical? The rest I will do it myself.

AIP: Is the 'artist's hand' important in your work?

JS: By principle and postulate I should say it is not important. However, necessarily it always ends up being important. Because no matter how much I tell an assistant how to draw something he will never draw it like I would. I'm now working on a series of paintings that are like a black silhouette. What I do is I draw the silhouette. It is a painful job to paint it all in black. So I do the outline and then my assistant fills it inside with black. But, that even a child can do. Still the exterior line the one that defines the black space is something I have to do myself.

AIP: I know that in the installation *Amazônia* from 1992 it was your assistant that drew the motifs... [88]

JS: In that work it was my assistant yes. I really wanted him to do the drawings. I did not want to do them myself.

AIP: Why?

JS: I wanted them to be authentically naive. And I could never do authentically naive, it would not be authentic. My assistant (a Brazilian from the countryside) did not chose what we were doing, I would say "…do this…" and he did what I told him to do but, in his own way. Therefore, the concept behind it was mine.

AIP: And in the work done for the exhibition *The House with the upstairs in it* in which your son draws part of the work? [88]

JS: There are several, it is not just one. It wasn't draw by my son. It was made from a drawing my son did. I made a slide of his drawing and projected it in a paper and asked an assistant to draw it as such. Using the slide we followed the drawing exactly like it was. Therefore, it was not made by

me, it is in fact based on something my son did. He was a baby by this time, around one year old. There are other works where the same principle was kept: drawing exactly as the projection of another drawing. I did not invent anything. The methodology was this: here you have an A4 paper, the drawing was projected on it and where there was no drawing, there was only the light of the projector, and where there was light, it was painted black.

1.2. Interview 2: 16th of June of 2008

Participants Julião Sarmento and Ana Isabel Pereira
At the artist's studio (Centro Empresarial de Sintra-Estoril, n.5, Armazén B-8)

The intention in the second interview was to clarify some issues from the interview conducted in 2004. Furthermore photographs taken in Sarmento's studio in 2004 showed paint tubes, bottles and cans that not only had been used by the artist but also had historical importance. Namely, old bottles of the Portuguese paint *Sabu* and paint tubes of the British paint *Rowney*. Both these PVAc paints have been discontinued and it was important to register and analyze them. The interview began with a talk on Sarmento's most frequently used binding medium the *Vulcano V7*.

AIP: Now in the market we have white glue *Bizonte* that replaced *Vulcano V7*.
JS: Yes but, the problem with the *V7* and it is the only problem is that it yellows and very quickly.
AIP: We are going to conduct some experiments with several pigments in order to assess the influence of pigment on that process. We want to see if titanium white and lithopone protect or not the polymer. We are going to start with the whites and the blacks as these are the colours that Julião uses.
JS: That would be good. Nowadays I am using a trick. Why? Because all the white paintings I have done were bright white and are now really yellow.
AIP: Even the recent ones?
JS: Yes, let's say the ones from around 2000 are already…orange. At the moment I am trying to do something. I am experimenting to see if I can surpass that because it is annoying me. On one hand I admit to the fact that there is a change of colour. On the other hand it irritates me because I wished they would remain white. Instead of having to admit the colour change I would rather not have to admit it and that it stayed white. So now what I'm doing is: I make the backgrounds exactly like I usually do with the PVAc and titanium or zinc white it depends…
AIP: If you are using the *Cenógrafa* white it is lithopone.
JS: And then what do I do? Then I paint with acrylic gypsum on top.
AIP: That was one of the questions I had. What is the brand of the acrylic gypsum?
JS: It is either *Winsor&Newton* or *Talens*, usually *Talens* because you can find it more easily. Acrylic gypsum does not yellow does it?
AIP: The acrylic is supposedly more stable than the vinyl. One of the issues we are trying to address is that. At this point of the research I am trying to establish the PVAc based paints that

can be found in the market. There are the *Flashe*, the *Rowney* of which Julião has some tubes…in fact I was going to ask if you can remember in which works you used the *Rowney* paints.
JS: No, I do not remember.
AIP: And the *Cenógrafa*pigments? They are now selling others is that it?
JS: Yes.
AIP: We tried to buy *Cenógrafa* but, they did not have it. The factory closed and their residual stock had run out. We found some in a little artists materials store downtown. They had some brought from their warehouse that morning. Fortunately there was still one bag of white and one bag of black *Cenógrafa* dry pigment. Another issue I need to clarify is that Julião in the interview in 2004 states that in the 80's you would have seldom used acrylics, right?
JS: Yes, it is true.
AIP: But the works done in 81 and 82 are all categorized as acrylics…
JS Ah, but that was with the paint…what was the name…from the *Casa Varela*…
AIP: The *Sabu*?
JS: Yes *Sabu*, that is it.
AIP: But the *Sabu* is PVAc based.
JS: It is PVAc?
AIP: Yes, it is.
JS: Because I asked them what it was and they answered it was acrylic tempera.
AIP: Exactly like they announce them in the catalogues.
JS: I am not sure if I told you on that previous interview but I had a sort of a law. Anything that I could find that was cheaper would be what I would use. And this is absolutely true, because this all started as a question of need. I did not have any money. And it is funny how at some point there was a lot of talk and writing on the fact that I used grocery paper, which I started using when I started painting. Besides liking this paper it was very cheap. I did not have a penny at that time; I did not have any money. Therefore I used the *Sabu* paints that were very cheap, that paper that was very cheap and what happens? Then I started to get used to using a certain kind of material. I would enjoy using some particular materials. In certain cases even after I started to earn more money I did not change because I liked using those materials, because I got accustomed to them. Still the only reason that all started was that I had no money and those were the cheapest materials that I could find in the market.
AIP: They are not necessarily of the worst quality. So, besides the yellowing do you notice other degradation problems in your works? Cracking? Or, is it only damage from handling?
JS: No, no cracking.
AIP: There are some paintings in the catalogue *Flashback* [88] with a green background that I think were made while Julião was in the Amazon. On the photographs you can see what appear to be cracks in the paint layers.
JS: I do not know about those because I do not have any with me.
AIP: There is one displayed in the Centro Cultural de Belém.

JS: Yes, there is one in CCB. Others are in Brazil and others are in private collections. Nonetheless I do remember at that time it was very different. The PVAc I used at that time was Brazilian and would crack much more than the one here. This one was much more elastic.
AIP: Do you remember the trademark of the one you used there?
JS: I am not sure if I ever knew. I am not even sure if there was a trademark. But, it was surely much stiffer than the one from here. *Bizonte* is much more flexible.
AIP: So you still use the *Bizonte* with the dry pigment?
JS: Yes, I buy bags that are much cheaper.
AIP: In 2004 Julião often referred titanium white. However *Cenógrafa* white is made of lithopone…
JS: Well they said it was titanium white. As they said that *Sabu* was acrylic.
AIP: On the photos from your studio one could see several cans of industrial household paint from Robiallac and Sotinco. Do you remember in what paintings those paints were used?
JS: I do. They are recent. They are over paper. A series called "What makes a writer great"[32]. It was all done with these aqueous enamels. I never used them on canvas only on paper.

1.3. Workshop at DCR – 3rd of May of 2010

Participants Julião Sarmento, Romeu Gonçalves, Maria João Melo, Ana Isabel Pereira, Joana Lia Ferreira, Leslie Carlyle, Master Students of Conservation and Restoration attending the Hystory and Tecnhiques of Artistic Production Lectures (academic year 2010/2011); Jorge Imaginário (video production)
At the Departmento de Conservação e Restauro, Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa, Campus de Caparica.
In May of 2010 Sarmento was invited to do a workshop for the Conservation and Restoration course in the subject History and Production of Art Techniques. The objective was the artist to show how the painting *Frozen Leopard* was made so that the students could do a reproduction following the artists instructions. The following transcription was made from the video produced during the workshop.

Julião Sarmento: Now I know that this is to reproduce the *Frozen Leopard*...Well let's see. I'm not a very disciplined person. I think it is very important to do this because I have seen a lot of mess even on an International level regarding my work and completely wrong ideas on how I work. It is usual to see the techniques description as 'oil on paper'. I should say I like oil very much. I have nothing against oil. I worked with oil during my course. But, I should say I painted two paintings in oil in my life. Two!
Maria João Melo: But, you like oil very much?
JS: but notice that I also like many other things that I do not use because they are not appropriate and oil is not appropriate for what I want. I am much faster than oil.
MJM: And it dries badly. It dries and spoils.

[32] The series *What Makes a Writer Great* was produced between 2000 and 2001.

JS: So, basic ideas that you must know about my work. From the beginning I adjust the materials to what I want to do. In general, however many other times I adjust what I want to do to the materials I have. I was always very inventive regarding the materials. Although I do not have a Jewish or Scottish bone it looks like I have one because I am very cheapskate. First I was cheapskate because I did not have much money. Now that I could spend more money I am still cheapskate because I still think it is not worth it to spend more. I have also listened to extensive dissertations and written texts why I would use this or that kind of paper, that pigment or, that glue. It is very simple I started using dry pigment and glue because it was much cheaper than buying acrylic paints. Then I thought that it would give effects that I with acrylic paints could not achieve. And I can get a 10mx2m surface that is the same price of a 7x7 in acrylic. This is pure economics.
MJM: We are finding that these older PVAc formulations are probably more stable than the acrylics. So, they would be cheaper, more stable and more suited for the technique.
JS: Already in the beginning of the 80's I would paint with grocery paper, a brown greyish paper (it is not paper wrap)...it looks like recycled paper only it is thicker. Why did I start to work on this paper? Because I could buy reams of this paper that would give me about four hundred or five hundred sheets of 1,20m, 186cmx102cm. And that would cost me...I do not know...about two hundred of those sheets would be the price of a Fabriano sheet. It's economics. So, all this because I adjusted, went adjusting my work to the materials I used instead of the other way around. I have a great friend (that you probably know) that is a Swedish-american artist that lives in Portugal and that is called Michael Biberstein and that is the opposite from me. It is funny to do this dichotomy. Because he wanted to do a painting this big [Sarmento shows with his hands a small square] and would spend tonnes of money. He would buy sable brushes of several numbers...he would buy the most expensive materials he would find. I was the exact opposite. I would use the cheapest brush I would find in Casa Varela that was bought by the dozen. These were recycled brushes made probably from horse hair with some tin around them and I would use that kind of material. Because I enjoyed it and then it became natural to enjoy using this kind of material.
MJM: From the Casa Varela?
JS: I used everything from Casa Varela because everything is cheaper there. It's not that I have a craze over Casa Varela. There is a very simple reason. When I went to the Fine Arts School of Lisbon a colleague from the course...well I first studied Painting and then Architecture...when I entered in the first year of Architecture one of my colleagues was a guy named António Varela and Mário Varela owned Casa Varela. He would make me cheaper prices for everything therefore I started buying everything in the Casa Varela. All of my materials were bought in Casa Varela and still are.
MJM: By any chance you do not know if Rodrigo, the PVAc...
JS: I must say that Rodrigo was not very clear on some things and regarding that...we were sort of slaves that were paid by the hour.
MJM: I thought he showed you everything.

JS: No he would show up there with the materials and none of us knew where he bought them. And I doubt he would buy them in the Casa Varela. Rodrigo was worse than me. He could go from here to Badajoz to buy cigarettes if they were cheaper there.
MJM: Well, Mário Varela told us that we went there
JS: I am not saying he did not. I am saying I do not know. Well…now you know why I go to the Casa Varela When I restarted painting...Ah...as restorers there are three fundamental periods you must know. Until 1974 I painted with acrylic on canvas, I would order the canvas or, bought already prepared canvas, of regular linen. I would order them from Casa Ferreira. But, then the Corbel opened in Praça do Camões. And me and Fernando Calhau found that the Corbel had opened and we went there and they saw two young artists and they started to make cheaper prices so we started going to Corbel. So we started to order the canvas from Corbel. Those regular and common ones of linen that were already prepared and then we would paint with acrylic on canvas. Until 1974 all my paintings, all except one or two that were on oil, were acrylic on canvas.
MJM: And the brand?
JS: Acrylic from Talens. We lived with the dream of painting with what the Americans painted but, here in Portugal there was none. And very frequently we would apply a basecoat on top of the industrial ground layer. We would apply one or, two coatings of acrylic gypsum also from Talens. And then the painting was with acrylic paint on canvas. All the works until 1974, except for a few from around 1969, end of the 60's...I should say that in the future you will not find many of my works from then because unfortunately, and you might already know, there were a series of accidents in my life that made me lose a great part of my work. One of them was...
MJM: The fire in Belém?
JS: Yes, but in Belém it was mostly photography works, works made in the 70's. I lost films, archives, photographs, negatives. Photographic work from the 70's from which there is nothing left. Not even the originals. Everything burned. The negatives and the positives were burned. Everything burned. So...but there were also many of my possessions...I lived between 1967 and 1974 in Rua Nova do Almada, I lived in Chiado above the store Casa Batalha, and I had there many things. I lived there with my second wife and then we split up and as usual she kept much of my stuff. I had there lots of stuff and many works from the 60's, paintings from the 60's that if they were not burned in the Belém fire were burned in the Chiado fire. But, there may still be two or three of those paintings left. They are exceptions, I made them in the end of the 60's around, 68, 69. At that time I would do a frame in pine that would be covered with a rigid surface that would be covered with platex. Therefore, it was a rigid canvas. Instead of being a canvas it was platex. And then I would paint on top of the platex.
Joana Lia Ferreira: Just out of curiosity on which side of the platex would you paint?
JS: On the smooth side. And normally at that time I would use...let's see if I can remember the name of the paint...I used household paints...
JL: Robiallac?
JS: No! That was very expensive.
MJM: Dyrup?

JS: No.

JL: There was a Portuguese brand named Soberana.

JS: No, it was even cheaper than that. Nobody knew it. It was a paint I discovered in a drugstore in Oporto. If I can find it out I will let you know. Well...then I would use that paint...for everything that I wanted to be dull to be matt I used that paint. Because I used to paint often in matt or gloss. What I wanted to be bright I would paint with Robiallac because it was paint with better quality. Because the other is too transparent.

MJM: And that is when? What is the period?

JS: Between 62-69. But, there are only two or three works from that time. Then I went back to painting with acrylic on canvas. Therefore, this was a period of 'rigid canvas' and then I went back to regular canvas, to linen canvas. In 1974 I abandoned in a desperate act...I completely abandoned between 1974...and this is strictly true (there was a period of overlapping when I did both things, photographs, paintings, drawings)...but between the end of 74 and 1981 I did not paint, I did not do a drawing. I made a half dozen sketches that were projects for installations but, they were more personal work, they were not considered works, right? Earlier I mentioned the forgers because some paintings have come out from 1978 and that is not possible, there are none. Well, by this time I worked only and exclusively with photography, with video, sound, with Super8 film, installations...ultimately on work that refers to mechanical reproduction. In 1981 with the triumph of David Hockney the painting fever returned and there I went to my friend's Mário Varela's place and set up a scheme with him. And then I restart the paintings you want to learn to reproduce. At that time there was a certain wearing out of the conceptual art or better yet of the pos-conceptual art because there was no conceptual art in Portugal...people, in generic terms went back to a sort of ground zero and things had to assert themselves by their dimension. People would paint very big things. And then between 1981 and 1983 I always worked on paper (if a canvas from this time also appears it is a fake because I never worked on canvas). I only restarted to work on canvas in 1983. In 1983 I made some failed attempts of buying canvas but, I was not ready for it or, felt like it because It was too much expensive. Therefore I used raw cloth, bed sheets and I still have some things painted in raw cloth. I would grab it, stretch it and paint it with *Sabu* paints. I arrived at the conclusion that the *Sabu* had a big yield, it was a sort of acrylic. I would buy them, I would have tons of *Sabu* bottles and that...

JL: It was super concentrated, you could dilute it.

JS: It was wonderful, I could use it for everything, to dilute...it would crack.

MJM: It would crack?

JS: Of course it did! It would crack badly. A thick, highly concentrated layer of *Sabu*...Casa Varela is not the utmost of refinement and I do not know how they would do that but, many times you would open a *Sabu* paint's bottle and the paint had a type of consistency and on the next week the same paint, with same colour, with the same reference, besides not having the same colour had another consistency. It would be either thicker, or denser...

JL: But it was not the same bottle?

JS: Obviously it would be another bottle. I mean it was not a smooth process. It would be dark pink but, it was not the same, it was not the same.
MJM: But, they were careful choosing the binder and the pigments were also quality pigments.
JL: Yes, but the complete formulation of the paint...
MJM: Yes, the final mixture was manual. However, the raw materials were good.
JS: Probably it was I believe that.
MJM: But, of course to apply a thick paint as long as it has fillers you can either go patiently applying layer by layer or, if we do as you imagine you doing...
JS: Wait a minute, that was painted with brushes...well, anyway this is all to arrive at the 'Frozen Leopard' that was what brought us here. In 1985 there is another shifting on working methods. That was when I started working with this PVAc, the *Vulcano V7*. I started thinking that in fact everything is a pigment and I started using lots of different pigments. If I grab all of you and stick you in Vulcano glue and paint you are pigments. People are pigments. Pigment is everything that can cling to the binder.
MJM: Well that should not be a great colour, right?
JS: Yes, but you can see my point. Fourty ruined chairs are pigment. In the end it is that, they are particles that are bound together by a binding medium. And then I started to think about it and got to the conclusion that if I bought...because I wanted to do really big paintings...and back then I searched in Oporto, in Rua da Conceição where a fabric store existed and got to the conclusion that in Portugal there was no raw cloth or canvas (to tell the true raw cloth, because by this time I could not afford canvas). It did not exist in Portugal and I believe it still does not exist, there was no canvas the size I wanted. Let's just say that the widest width I could find of that raw cloth in all the national territory was 1.50m. And I believe that this is still the case. And I wanted it to be wider. So I started (at that time I was working in Madrid) I started to order it from Spain. I arrived at the conclusion that curiously that cloth besides being of better quality than the one made in Portugal, I could buy a roll of cloth 2.15m wide and that roll would be cheaper than buying 5m of canvas with 1.,50m width here in Portugal. I do not understand how they would do it but, it really is much cheaper. Nowadays I still order the canvas from Spain.
MJM: But, is it made in Spain?
JS: I do not know. That is your problem. I do not know where it is made. I just know that it comes from there. I buy rolls of 2.15m wide, I buy that cloth and nowadays I like to work with that. It comes much cheaper.
JL: Just a question, you do not wash it?
JS: I do...no, I do not. I wet it. you will see in a minute how it is done.
MJM: And the firm from Spain, was it always the same?
JS: I have no idea.
MJM: Who does the order?
JS: It is Romeu.
MJM: Then we will later ask Romeu...
JS: No, we order from the galleries we work with. We say what we want and they get it.

MJM: But, it always comes from Spain?

JS: Yes, it always comes from Spain, sometimes from Barcelona, others from Madrid.

JL: Maybe there is a label and from there...

Romeu: There is usually no label.

MJM: Ok, we can try to figure that out later.

JS: But, notice that I got to the conclusion that it must be very easy to find that canvas because I use it since that time and ask for it from Barcelona, from Galicia. It never has the same thickness or colour but, it always has 2.15m and is always cheap. Which is fundamental. Moreover I have here some leftovers of canvas from that time to offer you. I even brought a Portuguese one for you to see the difference. So, this is the material I work with. Where was I? I started working with this and exploring...

JL: Earlier we were talking about pigment you started thinking that everything is a pigment.

JS: Exactly, and then I started thinking about what I could find in Casa Varela. And that was called...what was it...of Serigrafia.

AIP: From *Cenógrafa*?

JS: Exactly. During the 80'sI used those.

MJM: From *Cenógrafa*?

JS: Pigmentos of Cenografia. I even have here some from that time, the authentic and the legitimate. They are from when I painted with those colors. At that time I would do something I do not do these days because I started to be more careful with myself. At that time I worked a lot with my hands, I would do everything with my hands, I mixed the paints with my hands. But, then my skin started to crack and I started to wear gloves and after the gloves I started to use assistants. Ah…starting from 1990…I always had a much reduced color palette first because, the Cenografia brand did not have many colors. Then I would only use the colors I liked which narrowed even more the choice and then from 1990 I discarded colors and would only use white and black paint or, mix the white with the black. Moreover, the fact that I work with this Vulcano or *Bizonte* glue as with any other poly(vinyl acetate) (as you know) has a problem, it gets yellow. The paintings are bright white, of an immaculate white when painted and they turn yellow.

MJM: But, Rodrigo's paintings are not yellowed. At least Joana made measurements…

JS: But, the PVAc quantity in those is much reduced. In mine I would use a bottle of glue…the way I worked was for one of these 5liters bottle I would add 2Kg of dry pigment. It would depend but, in average it would be to packages of dry pigment and one 5 liter bottle of glue. What happens is that many of the White Paintings that by that time were very white nowadays are yellow. They have more yellowed areas, others whiter. Where there is more poly(vinyl acetate) it is more yellow. But, it does not bother me I know that it yellows.

JL: And Rodrigo's paintings have titanium.

JS: And they have a lot of water.

MJM: Even so they have a lot of binder, as much binder as regular paints.

JL: And they do not have fillers.

MJM: But, that is not turning too much yellow? It is only in the places where there is too much binder?
JS: Some are turning very yellow. I have some that are really yellow.
AIP: The painting that caught my attention was the painting Belém. However it is on display in a public space, near a café where people can smoke.
JS: For example, I have a friend that has a painting that is really yellow…it is turning "ochre".
MJM: If you wish it could be something that Ana Isabel could do in her Ph.D, testing some additives that you can add to the PVAc to avoid the yellowing.
JS: Lately there are some paintings that I do not want them to yellow…
MJM: This PVAc we think that is aging well because the new formulations are bad, they are bad for the artists.
JS: It is evident that all the whites will end up yellowing, right?
MJM: They have a bigger tendency to show that. However, the whites from Joaquim Rodrigo which are thirty years old are almost as white as Joana's reproductions.
JL: Forty years old. Yes, most of them. However there is a case where it turned yellow.
MJM: But his white is made with titanium white.
JL: Yes, it is that titanium white is very white. Even if the polymer has a tendency to yellow as the pigment quantity is high…
JS: And the *Cenógrafa* white is made of what? Is it zinc?
AIP: It is lithopone. It has barium and zinc.
JS: Well when you look at art this technically…It is a good thing you exist but, then I begin to wonder if you think too much about this you end up doing nothing.

Reproduction of a painting from the 80´s

JS: First we need to wet the canvas and spread it on the plastic to remove any bubbles. I would always use a plastic underneath. That is why all my canvases have 'rivers' on the back, which are marks from the plastic. However, all is premeditated. I am going to do it like I did in the 80's.
Leslie Carlyle: If you have a very large canvas how do you wet it?
JS: Well it depends usually I would pour water and then spread it with my hands. Or, I would use a piece of wood.

Fig. A1.1: Images of Julião doing a demonstration of how the paintings from the 80´s were done. a)The cotton fabric was wetted and stretched over plastic. b)- Glue was poured directly over the canvas. c)- Dry orange pigment was dropped directly over the glue. d)-To mix both Sarmento used a spatula and then his hands. e)- At some point more glue was added. f)- To demonstrate one of the ways used to obtain a flat surface Sarmento spread water over the surface. g) – the paint was smoothed out with his hands.

MJM: You use the glue like that, directly without any dilution?

JS: Yes, absolutely.

MJM: But, it looked like there was so much pigment.

JS: Now, all of this would change according to the thickness I wanted. If I wanted it to be thicker I would do it like I am doing. If I wanted it to be thinner I would mix more water. Or, what I would also do was to dilute the glue and add extremely diluted glue. There were many ways to do it. It would depend on what I wanted. Sometimes I would want an entirely different surface and would drop water on it and that would give you a completely different surface. Other times I would go on top of a ladder and I would just dribble the water drop by drop and that would make craters, little craters on the paint. Nevertheless this is the typical surface from the 80s. There is nothing more or less simple than this. Other times if I wanted to be more ingenious I would take earth, I would go to the garden grab some earth…

MJM: And you sifted it?

JS: No. I would just throw it on the surface and mix it all together. It depends on what I wanted. If I wanted to swift it I would. I had a big garden and many times many of these paintings from the 80´s were made in the garden, were made on top of the ground. And it would be wetted with the garden's hose.

MJM: But, it is true that the texture is a characteristic in all your works?

JS: Yes and the texture is created using paint like this. However, with the white canvas the so called White Paintings the strategy is already a little bit different.

MJM: And now you will leave it to dry like that?

JS: Yes, I will leave it to dry. My production in the summer was always bigger…

MJM: You would not use the drier?

JS: No, I would never use the drier. That is too much trouble. Just let nature take care of things. After it dried it would be time to draw. Many times when the works are described I would say mixed media on canvas because there is "stuff" in it.

MJM: And you always do it on the floor?

JS: Always.

MJM: And the drawing you would do it on the ground or, with canvas in a vertical position?

JS: Usually, usually the drawing is made with the canvas standing up. Usually…however as everything in life I do not have any rules. I am completely devoid of rules. That does not mean that once in a while I will not do draw one with the canvas lying down. The paintings were always done with the canvas flat on the floor for obvious reasons. Many times this would dry and I would paint on top with *Sabu* of course. Sometimes with the *Sabu*, sometimes with paint made from this but more diluted. And those were many times done horizontally other times vertically.

MJM: And the stretcher? Would you stretch it before you draw?

JS: Stretching is the last thing. It is the last thing to be done.

Student: Does the canvas shrink when it dries?

JS: Of course it does and it shrinks a lot. That is why the stretcher is the last thing to be done. Only after it is all painted and has dried would I put it in the stretcher.
The White paintings are worked in many ways, according to the surface I wanted to obtain. The question is that it all depends on what I wanted. At times I wanted the surface to be very even and I would do it a certain way. I would do it another way if I wished the surface to be more uneven. If I feel like having a particular texture I will do it another way. On the White Paintings I did not do it as the paintings in the 80's. I have a bucket and an industrial blender. I just pour the glue in the bucket, pour the pigment and mix it. Many times until the mixture is completely homogeneous, that is a completely homogeneous paste and then…It all depends on what I want. There is only one way to get there yet the results are all different. Many times the paintings have areas were the canvas is showing through. The support was really wet, almost soaked, with pools of water. When I pour the paint on top, on the areas where there is too much water the paint will be much more diluted. Therefore when it dries you can see the canvas. I can take the pigment mix it carelessly and the paint will be full of pigment lumps. Or I wish it to be thoroughly mixed thus I blend it until it as a creamy texture. Hence, I control the final result. By making my paints this way I have control over everything in it. And this is always different that is why it is so difficult for me to explain how it is. The paint is always different, sometimes it is more liquid other times it is thicker, sometimes is more homogeneous.
MJM: And on the *Frozen Leopard*?
JS: On the *Leopard*…well the bottom piece is made with this white pigment. The upper piece is made with a pigment bought in Morocco, in Marrakech. I bought it on the street.

Julião Sarmento drawing

Unfortunately there was no mock-up of a highly textured paint on wich Sarmento could demonstrate how he created the drawing. A piece of hardboard with a titanium white paint layer on top was used for that demonstration.

MJM: So you use graphite pencils?
JS: I used graphite sticks.
AIP: We have those. Do you prefer them softer or…
JS: Softer, those that are soft and smudge a lot.
MJM: And the graphite do you also buy it in Casa Varela?
JS: No, the graphite was where I could find it.
MJM: But, would you not always buy your materials in Casa Varela? Does it also depend?
JS: Yes, on the graphite surely. Let's see, if you now approach this drawing you will see that here on the side of the shape are starting to appear "ghosts". They usually appear and result from your hands getting dirty from the graphite powder. If I make another form here on the side you see the "ghost" of the previous tree.
MJM: Do you let those stay or, do you take them off with a brush?
JS: No, this is part of the process.
AIP: And after you apply something over the drawing like a fixative?

JS: Nowadays I apply fixative. Back at those days it would be hairspray *Elnettt Satin*.

AIP: But, the paintings would smell like a hairdresser…

JS: Yes, they would smell like a hairdresser. That was the problem. But, it was cheaper. The less expensive one I would buy was in *Continente*.

MJM: But, you only applied it over the drawing?

JS: Yes. The hairspray is a fixative.

Of course that when you are drawing over a highly textured surface, over a canvas, there is much more powder and the line is not so regular. It is completely different from what is happening here obviously.

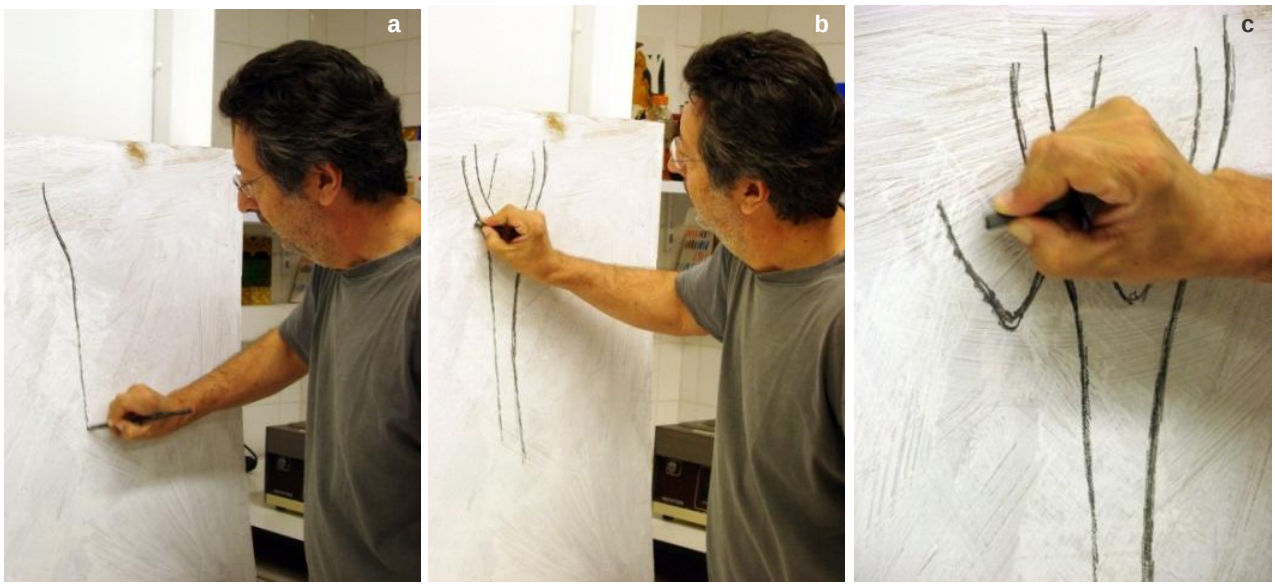

Fig. A1.2. Julião Sarmento exemplifying how the graphite drawings were made. a) and b) Soft graphite sticks are used to sketch. c) As Sarmento places his hand on top of the outline the loose graphite is dragged and leaves marks on the surface.

The third phase of the workshop was dedicated to the creation of the white background from Frozen Leopard. This should be the typical method used in the paintings from the 90´s. Sarmento had already transferred some of the Bizonte glue into a new plastic container and was ready to add the dry pigment when he began his explanation.

JS: Ok…so here is where the artist's soul resides and there is something that is very important that is the mixture, the proportions. Those depend on what I want. The proportion between the pigment and the glue is not always the same. And I would usually dilute the glue with water.

Julião mixed the pigment and glue together and then added some water. Meanwhile his assistant prepared the canvas as before. It was wetted in a bucket with water and stretched over the plastic that covered the floor.

JS: I do not usually use water at this point. I would do another thing. Making it just like I used to do I would dilute the glue with water and would mix it up slowly. A good consistency is that of "chantilly". The water is added up slowly just like if you were cooking.
MJM: Did you do some experiments? In smaller canvas so you would see how the effects could be achieved?
JS: Sometimes yes.
MJM: So this was the texture you liked?
JS: That I liked? Well I think this is the effect that you are looking for. To reproduce the *Frozen Leopard* it would be something like this. Now I have to ask you all to move away. Romeu can you go outside and bring me some soil?
MJM: If you need some sand we have it
JS: No, I do not want sand. I want soil. You do want the *Frozen Leopard* right? The advantage of these processes is that every single thing will give a different experiment.
MJM: And the soil did you start using it in these white paintings for a particular motive?
JS: Sometimes I would look at them and it seemed to white. It bothered me.
MJM: But, why soil?
JS: Because it was right there to be picked up.

At this point Romeu had picked up some soil from outside and putt it in a bucket with water. Sarmento speckled this mixture over the paint's surface with his hand

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JS: There you have the *Frozen Leopard*. It is done. Now you just have to leave it drying. There are things that I never do in the real world and ended up doing here in the demonstration. For example, here you can see the marks left by my hands and fingers. In real life I never let that happen. I could spend half an hour concealing it all.
MJM: But, how do you disguise it, with your hands?
JS: Yes, at this point…I remember very well of *Frozen Leopard* it was all made by hand.
JL: But, how do you reach the middle of the painting when a canvas has two meters by three meters?
JS: I start…I put myself on top of the canvas and start to apply on one of the ends and work my way to the other end.
Student: Do you have problems with drying?
JS: No, because this will be dried…I do not know what is the environment like here…however, with this weather, with this temperature, tomorrow by this time it will have dried. It dries fast but, not so fast.
MJM: So, the painting will dry and then you put it right away in the stretcher?
JS: No, the stretcher is the last thing to be done.
Student: So how do you do the drawing in the vertical if the last thing to be done is putting it on the stretcher?

JS: Because I staple it to the wall. I grab the canvas and staple it to the wall. However, sometimes I would do it on the ground it depends. It is also important that you know that in the 80's…I only stretched canvas until I could afford someone that would stretch them for me. My first assistant only had one job (and by the way it was a [female] assistant) that was to stretch the canvas, nothing more. Because after stretching around 500 canvases I was tired of it. These days it is Romeu that stretches the canvas.

MJM: So, besides soil is there any other material you use to do these effects?

JS: Usually I prefer what is most at hand. I have done it with many other things but, it depends. When I say it depends I mean of the circumstances, of the occasion. I want you all to understand one thing and this is essential and if you think of my works in these terms it is easy to figure it out. I am highly permissive regarding the materials I use. I mean there are no taboos on the subject of materials. Therefore if at some point I find that I want to put sticky tape in there I will put sticky tape in there.

MJM: And then you don't apply any finishing, it is only the hairspray protecting the drawing?

JS: Yes and nothing more.

Fig. A1.3. Images of Sarmento reproducing the white background of Frozen Leopard. a) *Bizonte* PVAc glue and *Cenógrafa* white pigment were both added and mixed in a bucket until the desired consistency was achieved. b) The cotton fabric was wetted and stretched over plastic. c) The white paint was poured over the wet and bare cotton canvas. d) The paint was spread over the surface manually. e) The final appearance of the paint before drying.

1.4. Short conversations 1 – at 3th of January of 2011

AIP: About the painting *Salto*, from 1985-86, paper glued on canvas. We are having difficulty in the identification of the glue and the paint seems to be impregnated by a substance which we are also having difficulty in identifying. Do you remember the kind of glue used to attach the paper to the canvas?

JS: When this work was painted there was no intention to have the paper glued to any support. It must have been glued by the owner without discussing it with the artist.

AIP: Did you apply any ground layer on the paper before painting on it?

JS: The paper had no kind of preparation prior to painting it.

AIP: The *Cenógrafa* white is no longer being produced and in one of the visits I made to your studio you told me that you still used a white pigment that you bought at Casa Varela. Is it possible to provide us with the reference or, brand of this pigment? We have to use the same pigment in the next laboratory reproductions.

JS: This pigment is bought by weight (it doesn't have a reference). Two types are used: a titanium dioxide and a zinc white.

AIP: Could you tell us when you started using this new pigment?

JS: From 2008

AIP: Regarding the application of a thin layer of acrylic gypsum over the layer of *Vulcano V7*/white pigment. Can you tell us when you started to use this new technique?

JS: From 2004

AIP: How much time do you wait before applying this upper layer?

JS: It varies. Normally, the least amount of time possible…as soon as it is dry.

Appendix Ib: Interviews with Julião Sarmento (in Portuguese)

1.1.Entrevista 1: 12 de Janeiro de 2004

Participantes Julião Sarmento e Ana Isabel Pereira

No atelier do artista (Centro Empresarial de Sintra-Estoril, n.5, Armazén B-8)

A primeira entrevista a Julião Sarmento foi realizada em 2004 durante o Projecto para obter o grau de Licenciatura em Conservação e Restauro.[19] O Projecto tinha como objectivo o estudo da pintura *Just a Skin Affair* feita em 1988. Para além de se pretender obter informações relativas a esta obra em particular as questões foram planeadas com uma abordagem mais geral. As questões direcionavam-se a obter a descrição e opinião de Julião sobre os seus materiais e técnicas e a sua opinião sobre a preservação do seu trabalho. A informação que foi recolhida naquela altura foi essencial para a investigação conduzida agora de modo que foi considerado importante ser aqui incluída.

Ana Isabel Pereira: Numa entrevista a Germano Celant [88] diz que a "pintura é simplesmente uma ferramenta e uma maneira de exprimir algumas ideias… Porque finalmente os objectos produzidos por mim, apesar de serem feitos em telas e de terem o aspecto tradicional das pinturas não são exactamente pinturas, pelo menos para mim não o são." O que quer dizer exactamente com isto?

Julião Sarmento: É preciso contextualizar as coisas… o contexto em que isso foi perguntado refere-se ao conceito da obra, da própria criação da obra. O que é um facto é que não são pinturas porque a pintura como essência não é aquilo que me interessa… o que eu procuro quando faço um quadro não é a pintura em si, a pintura não é um fim, é apenas o meio para chegar a um lado qualquer. Enquanto temos pintores tradicionais, como por exemplo, Kieffer ou Baselitz, ou os Novos Expressionistas Alemães, ou alguns pintores ingleses como Per Kirkeby, ou a Paula Rego…a pintura deles é um meio e é um fim. Portanto, o fim desse meio é a pintura. Para mim a pintura é apenas um meio para chegar a um fim, o que me interessa a mim não é o quadro, é o que é subjacente à pintura. Digamos que entre dois tipo de escolas... Aquilo que o Baselitz representa numa escola de pintura, eu identifico-me muito mais com o Polke, que utiliza pintura, mas que para ele a pintura também é um meio não é um fim, não é um pintor como Baseliz é. O Polke utiliza a pintura como estratégia. No fundo é isso que eu faço…estratégia não no sentido de táctica mas, no sentido de meio.

AIP: Quando se faz uma síntese das suas obras encontra-se uma grande exploração e combinações das matérias e de técnicas: tela (desengradada) e papel; colagem sobre papel e tela; colagens e madeira; tela e madeira; tela e plástico; fotografia e madeira; tela, zinco e madeira; chumbo, madeira, fotografia, vidro acrílico e tela; tela, cortiça e madeira; colagem e platex; madeira, terra, grafite, ferro e cartão; tela e pepel emoldurado sobre acrílico; ferro, chumbo, pó de pedra, acrílico, madeira, cola, tela, grafite. Do mesmo modo que para alguns artistas os materiais que usa tomam um papel ao lado da forma e da cor?

JS: Tomam. Refere-se se tem um determinado peso? Sim, tem um determinado peso…

AIP: David Smith (1906-1965; artista americano) afirmava em 1959 “A verdadeira pintura a óleo é um acto de cultura elevada… é o fruto de anos inteiros de uma longa e metódica aprendizagem, é preciso aplicação no desenho, trabalhar aguarela, aprender a fazer esquiços, é preciso compor- tudo actividades que necessitam de um material especial e muito secreto. Assim que me rendi a Nova Iorque e Paris, foi para descobrir qua a pintura se fazia com tudo o que apanhássemos à mão- telas grosseiras ou preparadas, com ou sem pincel, por terra ou no cavalete; não existem regras e não existe material secreto, não existe mais nada senão a convicção do artista”. Que comentários faria sobre esta afirmação?

JS: O único cometário que tenho a fazer é que estou inteiramente de acordo…é rigorosamente isso. Não lhe acrescentava uma vírgula.

AIP: Nesta (e na maior parte das obras observadas) nota-se que cada tela tem cores, “traços” e superfícies (em termos de textura e brilho) muito diferentes; cada elemento é pintado de forma diferente, pinceladas grossas e esquemáticas; pinceladas mais finas e regulares; e superfícies uniformes com trabalho de claro-escuro. Isso faz lembrar o que Maria de Corral dizia em relação à pintura nos “Anos 80” “pela necessidade da figura e da imagem, do gesto pictórico…pelo prazer de pintar, o gosto pelo pigmento e pelos materiais “. Na sua opinião, existe nestas obras essa relação?

JS: Sim e não. Esta a falar de três obras que são de épocas completamente diferentes, *Noites Brancas* que julgo ser de 81, ou 82, *Just a Skin Affair* de 1988 e *An Involved Story* que é de 98… e o *Frozen Leopard* de 93. Essa afirmação aplicar-se-ia mais à obra de *Noites Brancas* que é de 1981, porque nessa altura tinha uma atitude muito experimentalista em relação às matérias no fundo era… um pouco de vir de encontro com essa afirmação de David Smith: se por um lado, tinha essa atitude experimentalista com os materiais e dava-me imenso gozo experimentar os materiais novos por outro lado, também utilizava todo o que tinha a mão e que me fosse fácil conseguir, que fosse barato, porque nessa altura não as possibilidades económicas que tenho hoje em dia e servia-me disso como estratégia e utilizava os materiais de pouca qualidade e baratos. Para compreender melhor a situação eu vi-me obrigado, por razões exteriores a minha própria existência da prática artística, não porque assim me fosse determinado artisticamente, vi-me obrigado, por razões económicas, utilizar materiais paupérrimos e baratos. Isto porque não tinha outra hipótese mas, por outro lado, também não seria isso o impedimento para fazer aquilo que eu queria fazer. Portanto, adaptei todo aquilo que queria fazer as hipóteses que tinha de aquisição de um determinado material e habituei-me a trabalhar com materiais correntes. Nunca fui um artista, e mesmo hoje que poderia fazer isso, que utilizasse materiais caríssimos e pinceis de marca… não me da gozo. Apetece-me trabalhar, transformar coisas que não valem nada em coisas que começam a valer muito. É um pouco isto se quiser… mas, nessa altura tinha vindo de um período complicado dos anos 70 e princípios dos anos 80, fundamentalmente dos anos 70, de uma base muito teóricas, de um trabalho consistente… toda aquela fase de obras conceptuais que, as paginas tantas eram tao previsíveis que me irritavam, isso correspondeu mesmo a altura em que recomecei a pintar nos inícios dos anos 80, portanto havia muito o sentido do exercício da

liberdade. E isso foi o que me levou a experimentar as coisas… o que tinha a mão, embora às vezes se fosse preciso andava dois metros para procurar uma coisa mas se fosse possível não andava dois metros… e depois adaptava aquilo que queria fazer com as coisas que tinha.

Materiais e técnicas

Tintas

AIP: Apesar da minha observação se ter centrado nas quatro obras que são propriedade do CAM gostaria, que me falasse das tintas que usa e que já usou ao longo tempo.

JS: Eu já usei imensos tipos de tinta. A tinta que menos usei até hoje, fiz para ai 3 a 4 obras, foi o óleo. Porque o óleo demora imenso tempo a sacar e eu sou muito imediato, não tenho muita paciência… de facto nos tínhamos quase um dogma, éramos artistas do seculo XX e o óleo?!... Depois habituei-me a trabalhar com outro tipo de materiais. No início dos anos 70 trabalhei fundamentalmente com acrílicos depois trabalhei… "eu estou a fazer assim uma espécie de resumo sem entrar em detalhes"… quando deixei de pintar por volta de 1974 comecei a trabalhar com fotografia, filme, vídeo e com som, etc… com materiais reprodutíveis digamos. Quando recomecei a pintar comecei a usar têmpera acrílica, trabalhava com tintas *Sabu* da *Casa Varela*. E depois comecei a usar pigmentos com PVA, fazendo as minhas próprias tintas, misturando pigmentos com PVA. Os pigmentos podiam ser desde pigmentos industriais que se compram, desde de pigmentos que eu próprio fazia com lixo varria o chão e era o pigmento…

AIP: Referiu numa entrevista a Germano Celant que fabricava a sua própria tinta de modo a poder criar diferentes tipos de tinta, de facto, as análises feitas até agora na pintura *Just a Skin Affair* revelam que algumas das tintas utilizadas foram feitas por si e nas quatro pinturas do CAM é evidente a exploração de tintas com diferentes características visuais. Numa mesma obra encontro camadas mates, camadas muito brilhantes; e encontro um "jogo" de contrastes entre estes aspectos. A questão é como é que as fabrica ou, ou melhor de que modo manipula as características das tintas?

JS: Isso depende de uma quantidade de coisas. Depende desde a qualidade do PVA que nem sempre é a mesma, a sua própria consistência com a diluição em água, muito vezes trabalho com muita água, outras vezes trabalho com pouca água, portanto diluiu muito ou diluiu pouco; misturo muito, ou não misturo nada os pigmentos. No fundo é uma técnica complicada… e não é complicada… é relativamente fácil de ser conseguida mas, tem uma serie de etapas. Se tiver um bocado de PVA e tiver um bocado de branco de titânio, por exemplo, tem enumeras maneiras de obter uma aparência diferente depois de seco, pode ficar brilhante, pode ficar muito mate, pode ficar lisinho, pode ficar granuloso. Depende da quantidade de água que adicionar, depende da maneira como mistura, se mistura mais se mistura menos. Utilizando a mesma quantidade de pigmento e aglutinante pode-se obter um resultado completamente diferente. Então se tiver quantidades diferentes é um número infindável.

AIP: Então a única coisa que utiliza para fazer as tintas são: o aglutinante, o pigmento…

JS: Aglutinante, pigmento e a água. De uma maneira geral, mas, não quer dizer que de vez em quando não faça outras coisas. Eu sou muito livre a trabalhar e não tenho dogmas se de repente

apetecer fazer uma coisa faço-a. Os meus quadros não são todos iguais em termos de técnica pode, eventualmente, aparecer um que tem outra coisa qualquer. Digamos que a uma base geral que uso em 90% das obras e que é o que eu expliquei.

AIP: Quais são a propriedades práticas e visuais que este tipo de aglutinante lhe proporciona em relação a outros tipos de tintas?

JS: A rapidez de secagem em relação ao óleo, o tipo de superfície que eu não conseguiria fazer com o óleo e o preço. Imagine o que era eu fazer superfície de $6m^2$ em óleo com aquele tipo de matéria, demorava meses, anos a secar, provavelmente, custava uma fortuna, e não conseguia obter o tipo de superfície que eu quero.

AIP: E em relação aos acrílicos?

JS: Em relação aos acrílicos normais de tubo? Eu não utilizo, pura e simplesmente.

Só utilizo acrílicos quando quero fazer uma coisa muito específica, relativamente pequena e com cores estranhas são difíceis de encontrar a nível dos pigmentos.

AIP: Já atrás referiu que usava diferentes qualidades de PVA, portanto nem sempre usou as mesmas marcas de tintas?

JS: Não, geralmente uso o PVA a *Casa Varela*, em boiões de plástico…

Nesta altura fomos ver as várias tintas que JS tem no seu atelier, das quais fazem parte, o PVA da Casa Varela; as tintas vinílicas Sabu; e tintas de fabrico industrial para pintura de interiores e exteriores – na recolha das amostras, será oportuno aprofundar a utilização os materiais.

AIP: Foi fácil encontrar informações sobre as propriedades práticas e sobre a durabilidade destas tintas?

JS: Nunca me preocupei com isso.

AIP: Conhece artistas internacionais e portugueses que usem o mesmo tipo de tintas e da mesma forma que o Julião o faz, misturando eles próprios o aglutinante e o pigmento?

JS: Sei que o Barcelló utiliza e não sei se ainda utiliza, o José Maria Sicilio utilizava, não sei se ainda utiliza… não quer dizer que não haja mais…e muito provável que haja mas, que eu não conheça.

AIP: Como é que geralmente aplica as tintas para criar os fundos?

JS: Depende… as vezes com brochas, outras vezes com pincéis, as vezes à mão, outras vezes com rolo, outras vezes com bocados de madeira. Depende do fundo que é. Outras vezes deixando que ela simplistamente escorra.

AIP: Geralmente tem a tela deitada?

JS: Sim, quase sempre… deitada no chão. Estendo a tela no chão e faço o trabalho no chão.

AIP: Nas obras presentes no CAM a criação dos fundos assenta numa progressiva sobreposição de camadas de tintas, as quais nem sempre acabam por aparecer na superfície. Por exemplo em *Just a Skin Affair* chegam a encontrar-se quatro camadas gerais e duas parciais. Costuma trabalhar assim, com muitas camadas?

JS: É muito possível… eu já a fiz há algum tempo. Nesta altura costumava trabalhar assim. Hoje em dia já não. Na serie *Pinturas Brancas*, já não é assim, uso as vezes duas no máximo três camadas, mas de uma maneira geral só uma.

AIP: Na serie de pinturas brancas a geralmente um diferença de brilho entre essa camadas?
JS: Têm. Mas, essa diferença de brilho na superfície é dada pelo que já falei pela mistura que é feita entre PVA e os pigmentos e a quantidade de água, etc… Mas, nessa altura eu pintava assim.
AIP: Porquê?
JS: Por muitas razões que vão desde eu não gostar da cor e querer alterá-la, até achar que esta é a melhor maneira de eu chegar a uma cor através de sobreposição de transparências, outra hipótese é a de poder encontrar na superfície diversos pontos de cor, de um maneira mais ou menos aleatória mas que coexistem numa mesma superfície. São tudo razões diferentes e neste caso não sei, já não me lembro. Havia ainda uma quarta razão. Naquela altura trabalhava numa grande quantidade de pinturas ao mesmo tempo e fazia, imagine um fundo pintado de amarelo e deixava pelo chão durante alguns meses porque, entretanto, o que queria fazer com esse fundo amarela, já não me apetecia, queria alterar e de repente tinha uma ideia para outro quadro que queria fazer mas, não precisava de amarelo, precisava de encarnado e então pintava por cima. Às vezes era uma questão de "reciclagem".
AIP: Era um trabalho lento no qual tinha de deixar secar as camadas antes de aplicar a seguinte?
JS: Em certos casos sim como, por exemplo, no caso que lhe acabei de dizer. Noutros casos, por exemplo, por razões muito objetivas era lento mas, não era assim tão lento. Como sabe isto seca bastante rápido. Às vezes eu não queria que secasse rápido e dava umas camadas por cima das outras, principalmente em camadas muito diluídas em que eu consigo a cor através de sobreposição de transparências, como por exemple *The Swifteness of Skin*, *The Boys Town*, e outras.
AIP: No geral, os tons das suas pinturas restringem-se a uma gama de terras, cinzentos, amarelos, verdes e, mais tarde o negro e o cinzento. Fica-se com a ideia que há uma certa preferência por certas cores.
JS: Há…Nos trabalhos que eu faço se exceptuarmos o início dos anos 80, em que houve uma altura muito curta, em que utilizei cores berrantes de encarnado, verde, etc.. Depois comecei a ter uma paleta muito mais reduzida apenas por uma questão de opção, não me interessam, acho que me distraem dos pontos essências. Começa-se a olhar para os amarelos, os cor-de-rosa, etc. que são importantes pra determinadas pessoas, para mim não são. E, hoje em dia, só trabalho praticamente com preto e branco.
AIP: Que tipo de pigmentos usa?
JS: De uma maneira geral uso pigmentos em pó. Às vezes uso pigmentos em concentrado líquido da *Winsor & Newton*, e da *Talens*, porque não há em pó ou, porque procuro uma cor mais intensa, utilizo aqueles pigmentos. Mas, aqueles pigmentos acompanham sempre outra cor, nunca são deitados só sobre o PVA, há sempre uma cor base, um branco que é "tintado" com aqueles pigmentos líquidos. Se deitar aqueles pigmentos directamente sobre o PVA, não sustem. O que vai acontecer é que ao secar o PVA, vai ficar uma massa transparente, esverdeada ou amarelada.
AIP: Eu presumo que os pigmentos em pó existem numa gama de cores mais limitada que no caso das tintas já preparadas.

JS: Claro que sim.

AIP: Isso não acaba por lhe limitar o trabalho?

JS: Não, por duas razões, porque como já expliquei eu tenho uma paleta muito limitada e as cores que existem resolvem-me a situação. Quando eu quero uma cor que não existe em pigmento em pó ou, quero alterá-la de certa maneira utilizo os outros. Não quero dizer que utilizo o pigmento em pó puro, tal como está na embalagem, daquela cor. Se eu quiser alterá-la, eu altero.

AIP: Nas análises feitas encontram-se camadas com um pequeno número de pigmentos misturados e outras em que o número de pigmentos é maior, mas que parecem resultar de uma "contaminação" com vestígios de tintas deixados nos recipientes onde as prepara. Portanto, geralmente utiliza os mesmos recipientes para preparar as tintas.

JS: Depende se eu quero fazer uma pintura mais de um modo mais "descuidado" com esta não me preocupo mas, se quiser fazer uma coisa muito pristina, por exemplo, se quiser um quando mesmo branco não faço isso como é evidente. É senso comum. As cores que se vêem nesta pintura, mais que cores, são cores sujas, que são conseguidas através de resíduos de outras coisas. Algumas vezes (não sei se foi este o caso) estava a trabalhar em sete ou, oito quadros, e eu trabalho com alguidares de plástico e às paginas tantas precisava de uma tinta qualquer e agarrava nos restos e juntava tudo. A cor era a que saía, era completamente aleatório.

AIP: As suas superfícies têm uma expressão matérica a qual é dada não só pelas tintas e pela forma como estas são aplicadas mas também, por vários tipos de textura criadas com a adição de matérias granuladas. Porquê e quando é que começou a usar estes efeitos de textura e matéria? Que materiais costuma usar para obter este efeito?

JS: Porquê?! Bem, isso já não é uma pergunta técnica. Porquê… porque me apetece. Fundamentalmente começou nos inícios dos anos 80… a superfície da tela começou também a ser palpável para mim, tinha de ser táctil para mim e interessava-me evidenciar as diferenças da superfície através disso, a estrutura da própria superfície da tela. Apercebi-me que podia alterar a superfície utilizando diversos truques como areias pigmentos mal dissolvidos, tabaco (tenho telas com tabaco, fósforos e pedaços de papel), pó de mármore que compro em Paris.

Suportes

AIP: Apesar de ter trabalhado com vários tipos de suportes como o papel e a madeira (contraplacado e platex) o suporte em tela parece predominar desde meados da década de 80 até agora. Porquê esta preferência pelo suporte têxtil?

JS: Porque tenho sido preguiçoso em procurar outro tipo de suportes. E não é bem tela, é aquilo que os ingleses chamam de "Cotton Duck" é algodão, porque junto o útil ao agradável. É incomparavelmente mais barato e tem uma coisa que o linho não tem, que é ter vida própria. O linho é mais estável. O algodão fica bambo quando está húmido, cresce e encolhe, e eu gosto que as pinturas tenham vida própria e que se alterem. Não gosto de coisas inalteráveis. Gosto de coisas em que se possa observar a passagem do tempo. E então…como nas próprias *Pinturas Brancas* o PVA amarelece, daqui a uns anos elas estão amarelas (algumas delas já estão amarelas) não ficam amarelo, amarelo tipo carro eléctrico, mas amarelecem. Eu tinha noção

disso, não é uma coisa que venha a descobrir mais tarde. Esse envelhecimento das coisas, essa alteração formal das coisas é algo que me interessa. Portanto, a questão de usar o algodão também tem, um pouco, a ver com isso. O suporte não é estável, de repente está mais bamba e depois tem de se esticar todo esse manuseamento constante das coisas é algo que me interessa a nível teórico.

AIP: Em pelo menos duas das quatro pinturas da colecção do CAM os suportes de tela são tensados na grade por si (ou por um assistente). Porque é que optou por este processo mais " tradicional" (no sentido de ser feito no atelier) de construção do suporte em vez de optar por suportes que são já comercializados e já prontos a serem usados?

JS: Todas as obras que estão no CAM foram esticadas por mim. Só há pouco tempo é que tenho assistente a fazer isso. Eu dava-me imenso gozo fazer isso. Mas, de repente comecei a ficar mais velho e mais mandrião e hoje em dia é o meu assistente que as estica mas, estiquei milhares de telas. Sou super maníaco que aquilo fique bem esticado. Para já não existem telas industriais em algodão, não há, só há em linho e em linho "preparado". Eu trabalho em telas não preparadas, trabalho no algodão puro, não utilizo aquilo que designam por "primed canvas" e depois a espessura das grades, eu trabalho actualmente com grade de 8cm de espessura, e isso não existe industrialmente. Eu sou um grande defensor da liberdade do atelier. Se me apetecer fazer uma tela com 77,8x99,7cm é isso que vou fazer. Não me apetece usar uma tela do tamanho que me dizem para eu usar.

AIP: E mandando fazer por encomenda?

JS: Todas as minhas telas são feitas por encomenda.

AIP: Quer dizer as grades?

JS: Sim as grades. Eu decido o tamanho de que quero fazer as telas e depois mando fazer as grades, tal e qual o tamanho que eu quero.

AIP: Trabalhando com telas de alguma dimensões, difíceis de manusear, com o têxtil a reagir à água do aglutinante, etc. tem necessidade de as tensar temporariamente? Ou seja, como é que o processo de ter uma tela solta onde está a pintar e ter uma tela a " mexer"?

JS: Não…eu só estico as telas quando ela está completamente pronta…depende… eu agora estou a fazer uma série de obras em que metade do trabalho é feito com a tela desengradada e a outra parte já com a tela engradada.

AIP: Mas, isso também acontece na *Just a Skin Affair*?

JS: Não, ela só foi engradada quando a pintura estava completamente pronta.

AIP: Mas, existem algumas camadas no elemento #1 que só se estendem até ao limite da superfície da tela, ou seja, não ultrapassam as margens da tela, indicando que há camadas que foram colocadas após a tela ter sido engradada.

JS: Já estou a ver… é que esta foi pintada de maneira diferente, foi pintada a pincel já engradada. E… já não me lembro… é a mais lisa?

AIP: Não, é a que tem mais textura.

JS: Sabe como é que isto foi feito. A tela foi muito bem esticada com algodão "puro", depois foi pintado na horizontal com um cinzento super bem dissolvido com o pigmento e PVA a criar uma

superfície quase como se fosse a textura de chocolate quente, ao mesmo tempo que é espesso se deitar sobre a superfície se espalha tudo, quando estava mais ou menos seco, com uma mangueira foi atirada água para o ar os pingos de água ao caírem sobre a superfície, provocavam isto…, portanto ele deve ter água suja com lixo … não, este não foi com isto, este era à "balda". Eu agarrava em água com pó do atelier … varria o atelier… e aquilo vinha cheio de pó, deitava para dentro de água e a água ficava castanha cheia de pó, depois molhava a mão e salpicava para cima da pintura. Portanto isto foi feito na horizontal.

AIP: De qualquer das maneiras, as telas estão sempre soltas quando as pinta?

JS: Sim. Mas, há excepções. Agora tive que "puxar pela cabeça" para me lembrar como é que ela tinha sido feita.

AIP: Alguns autores vêem a construção da pintura com a união de várias telas como modo de acentuar que o discurso é feito por "fragmentos da realidade" por vezes sem uma ligação aparente. Concorda com esta interpretação?

JS: Sim e não. Porque não têm que ser necessariamente fragmentos da realidade. Sim, por um lado é um sublinhado de fragmentação mas, por outro lado essa fragmentação não tem de ser de fragmentos da realidade. Portanto, sim até certo ponto.

Preparação

AIP: Em relação às preparações, já referiu que não costuma aplicar e não costuma utilizar telas já preparadas.

JS: Não é que não costume. Eu creio que nunca utilizei telas já preparadas.

Encolagem

AIP: Costuma aplicar uma camada de encolagem ou seja, uma camada que isole e torne menos absorvente a tela?

JS: Também não.

Vernizes

AIP: Porque é que as suas tintas têm características diferentes e a distribuição das tintas é irregular, a superfície das suas obras tem um aspecto muito pouco uniforme, o que sugere também que não utilize vernizes, visto que estes iriam regularizar e uniformizar a superfície?

JS: Não, nunca.

AIP: Mas, e no caso das pinturas onde usa grafite e giz (como as obras *An Involved Story* e *The Frozen Leopard*) utiliza algum fixativo?

JS: Uso… *Satin*, laca de cabelo mas, como as pinturas ficavam a cheirar muito a cabeleireiro comecei a comprar fixativo normal, da *Talens*, ou *Winsor & Newton*.

AIP: Mas, não se preocupa em fazer uma camada regular?

JS: Não, não me preocupa em fazer uma camada regular, é só sobre o desenho…depende, se for uma tela pequena dou a camada regularmente. Se for uma coisa gigantesca, não estou para isso, dou só no sítio do desenho. Como vê eu sou muito pouco ortodoxo a trabalhar.

AIP. Em relação a todos estes elementos de que estivemos a falar, poderia descrever as experiencias negativas ou positivas, mais relevantes, com os materiais e técnicas utilizadas?

JS: Negativas? Estas superfícies são extremamente cativas, no fundo o PVA é uma cola e se as pessoas não tiverem cuidado a manusear aquilo, já tive quadros praticamente destruídos porque vão para uma exposição qualquer e depois as pessoas embrulham aquilo em "plástico de bolas" (Bullpack), o que é que acontece… a superfície fica marcada com as bolas. Digamos que essa é a experiencia mais negativa. Tem de se ter extra cuidados porque a única coisa que se pode por ali em cima é "manga de plástico" vulgar que não cola. Mas, por outro lado também não pode ser prensado, porque se for prensado também marca, porque a superfície é constituída por minúsculas bolinhas transparentes. Se aquilo for prensado ficam as bolinhas todas esmagadas e a superfície fica muito mais brilhante do que deveria.

AIP: Mas, mesmo estando a camada seca?

JS: Sim, não cola assim mas, com as diferenças de temperatura e humidade…

AIP: Onde é que geralmente se abastece dos materiais (grades, telas, aglutinantes, pigmentos)? Já sei que pelo menos na *Casa Varela*.

JS: Sim, na *Casa Varela* compro quase tudo. Mas não é sempre. Vou à *Fernandes*…há certos materiais …sei lá. Isto é como ir ao Supermercado em que as pessoas vão fazer as compras do mês. Mas, depois preciso de uma coisa rapidamente não vou daqui para Lisboa, vou para um sítio mais perto.

Contexto

AIP: Em 1968, frequentava o curso de pintura nas Belas Artes em Lisboa. Numa entrevista dada a Germano Celant [88] refere que "queria pintar com acrílicos, porque tinha visto anúncios do *Aquatec* e de coisas parecidas. E descobri uma loja em Lisboa que tinha essas tintas acrílicas. Mas não estava autorizado a utiliza-las na escola, onde nunca ninguém tinha ouvido falar nelas, nem nunca se quer se tinham interessado por isso". Como era o ensino das Belas Artes nessa época, em relação aos materiais e técnicas de pintura?

JS: Depois de isso tudo ainda precisa de fazer essa pergunta?! Era isso…nós estávamos proibidos de usar acrílico. No meu curso…deixe ver artistas do meu curso que eventualmente você possa conhecer, pelo menos historicamente, o Fernando Calhau, a Graça Pereira Coutinho…(não me estou a lembrar de mais ninguém, o resto foi tudo para professores se não estou enganado). Bom…e nós não eramos autorizados a usar…tínhamos de utilizar tintas de óleo, têmperas de ovo feitas por nós, o que tem graça a pessoa fazer as suas próprias tintas… se calhar foi por isso que depois comecei a fazer as próprias tintas. Mas, parecia uma escola do século XIX, rigorosamente. Tínhamos aulas de técnica de vitral. Aliás não vale a pena continuar por aqui, porque era uma desgraça.

AIP: Nessa época era difícil de encontrar tintas acrílicas ou, sintéticas no comercio?

JS: Era.

AIP: Geralmente onde é que as encontrava?

JS: Fundamentalmente na *Corbel.*

AIP: E era só a *Aquatec* que encontrava?

JS: Era…não, a *Aquatec* nós só víamos o anúncio nas revistas americanas cá não havia *Aquatec*. Cá a única que havia era a *Talens*…não me lembro bem, mas julgo que era a *Talens*.

AIP: Porque é que estas tintas lhe despertavam o interesse?

JS: Porque eram as tintas com que trabalhavam os artistas todos que nos gostávamos! Os artistas Pop americanos e ingleses dessa altura. Trabalhavam com tintas acrílicas e esses eram os nossos heróis. Essas coisas fazem-se sempre por simpatia, não é?

AIP: Não o preocupou o facto de serem "materiais" novos dos quais se desconheciam as suas características e durabilidade?

JS: Não, pelo contrário até gostava!... Nós gostávamos de trabalhar com coisas que não conhecíamos.

AIP: Na mesma entrevista refere que chegou a fazer com um amigo "uma pintura acrílica". Lembra-se das diferenças que encontrou entre esse aglutinante e as tintas "que era recomendado a usar" no curso?

JS: Lembro-me que estávamos doidos com aquilo porque aquilo secava num instante, era plástico, ficava agarrado às coisas. Era um gozo.

AIP: Em 1969 é assistente de Joaquim Rodrigo (4), ano em que este mudou de técnica e materiais passando a usar o platex como suporte e "tintas" de natureza vinílica, mais propriamente cola branca *V2*, com uma gama restrita de pigmentos em pó, os quais tinham (segundo o próprio artista) uma carga simbólica. Esta escolha de aglutinantes e pigmentos do JR teve alguma influência no seu trabalho?

JS: Eu não sei…já me fizeram essa pergunta e eu não lhe sei responder. Por um lado, o Joaquim Rodrigo era o maior chato que existia na humanidade mas, um chato insuportável e maluco, completamente doido. Eu hoje em dia olho para o Joaquim Rodrigo de uma maneira que não olhava naquela altura. Eu naquela altura queria ver-me livre dele portanto acho muito estranho que me deixasse influenciar pelas técnicas do Rodrigo. Mas, por outro lado, há de facto coisas que coincidem…se foi de uma maneira consciente ou inconsciente não sei bem. Agora que…por exemplo, aquele interesse pela utilização de pouca cor, eu creio que sou capaz de ter herdado dele mas, também não sei. Se eu não tivesse trabalhado com o Joaquim Rodrigo não sei o que é que eu seria hoje em dia, percebe? Não tento entrar um bocado em esquemas de futurologia. Agora, eu acho que sim que é capaz de ter tido qualquer tipo de influência, qual não sei, mas é capaz de ter tido.

AIP: Mas, e em relação a este fabrico das tintas pelo próprio artista?

JS: Ele ensinou-me isso. Mas, o que ele me ensinou foi que se eu fizesse as tintas…ele não me ensinou, fui eu trabalhando lá…as coisas eram muito mais baratas e, isso era o que me interessava. Era uma questão de economia, de facto. Eu não partilhava os postulados do Rodrigo e aquelas loucuras todas e só há três cores, o encarnado e o preto, etc. Nós fartamo-nos de rir. Mas, o que eu via, trabalhando para ele, é que se eu trabalhasse fazendo as minhas próprias cores era mais barato do que se comprasse as coisas industriais.

Sobre *Just a Skin Affair* de 1988

AIP: Nas análises feitas os resultados apontam para o uso de PVA, o qual poderia ser então o *V7*, da Casa Varela?

JS: Nesta pintura em particular, eu não sei. Pode ter sido esse como outro qualquer. Mas, era PVA, disso não há duvida nenhuma.

AIP: O que é que usou para obter a camada castanha do elemento1?

JS: Isso é lixo. Eu varri o atelier (quando fiz isto tinha um atelier em Sintra, no meio do campo) onde entrava pó e lixo normalmente. E eu varria o lixo do atelier e ficava com um pó castanho misturado com troncos e "bodegas", era lixo. E depois agarrava naquilo e tinha uma peneira e peneirava o lixo e de todo aquele lixo obtinha um pó fininho, ligeiramente mais grosso que farinha…ha! Não, isso foi para outra coisa…Aqui, agarrava nesse lixo todo tal e qual como saía da pá e deitava para dentro de um balde com água, mexia e ficava tipo café sujo e depois atirava para a tela. Portanto, isto devem ser terras.

AIP: Esta camada mantem o aspecto original?

JS: Sim, tal e qual.

AIP: Um pouco atrás quando falava do lixo estava a referir-se à pintura *Dez Anos, 1986/1996* (exposição *The house with the upstairs in it* em Londres, em 1996)?

JS: Exactamente. Eu durante dez anos varri o atelier e depois fiz pigmento com dez anos de lixo.

AIP: Então para além da *Just a Skin Affair* e a pintura *Dez Anos,1986/1996*…

JS: Nesta altura era muito frequente utilizar lixo. Mas, não como nessa. Nessa altura dos *Dez anos* eu fiz um pigmento requintado com lixo. Eu durante dez anos varri o lixo…pó, não é lixo é pó, porque eu peneirava até aquilo ficar um pó muito fininho. E depois enchi um recipiente cheio desse pó e misturei com PVA tal como se fizesse uma tinta de uma cor única só que o pigmento resultava de dez anos "

AIP: E isso está relacionado com trabalhar com o que tiver à mão? Ou, tem algum significado mais específico?

JS: Nessa *Dez Anos* tem, se então demorei dez anos a fazer isso.

AIP: Porquê a preferência pelo branco de zinco quando o branco de titânio já o havia substituído e apresentava vantagens como a maior opacidade?

JS: Eu mando o meu assistente à *Casa Varela* e uso o que ele me traz. E é o que eles metem no pigmento de cenografia. Se uma vezes metem pigmento de titânio se noutras metem de zinco…

AIP: A disposição das três telas foi mudada após a execução da pintura, mas antes das tintas terem tido tempo de secar. Acontece-lhe frequentemente mudar de ideias na articulação dos vários elementos?

JS: As tintas tiveram tempo para secar.

AIP: Mas, existem marcas…

JS: Eu sei. Mas, é exactamente isso que eu lhe estava a dizer. Ao fim de um ano de elas estarem secas você junta-as e basta um dia de calor e elas colam.

AIP: Mas, estas marcas indicam que as telas já estiveram na posição contrária a que estão agora (mostrei a fotografia onde se viam as marcas deixadas pelos elementos metálicos de fixação)

JS: Não, não esteve inicialmente aqui. O que aconteceu foi que...estas placas de ferro não fui eu que pus. Quando a Gulbenkian a comprou isto ia tudo separado. Na Gulbenkian ela foi montada mal. Quando eu vi que estava errado fui lá e então nessa altura mudaram. Portanto, isto deve ter estado aqui (do lado contrário ao qual se encontra agora). Aonde as telas se colam é nos topos. Se você juntar esta tela com esta, passados quinze ou vinte anos, num dia como hoje não acontece nada, mas se estivermos em Agosto vão colar.

AIP: Então tem logo uma ideia bem definida de como é que se vão coordenar os elementos?

JS: Tenho, absolutamente. Eu quando estou a trabalhar os elementos, antes de eles estarem engradados, podem haver alterações. Mas, a partir de um determinado ponto é absolutamente claro. Eu quando mando fazer as grades já está tudo planeado.

Existe uma separação entre os elementos o que faz também com que a obra não seja um rectângulo perfeito. JS reparou quase de imediato nesta alteração a partir das fotografias que foram usadas ao longo da entrevista. A pergunta feita foi se o incomodava aquele "desnível" entre as telas, à qual ele respondeu que sim, que o incomodava.

Durabilidade e Conservação

AIP: Erich Gantzert-Castrillo (conservador-restaurador) do Museu de Arte Moderna de Frankfurt afirma que "Os artistas enfrentam muito mais questões de durabilidade dos seus materiais e espera-se que eles providenciem respostas". Aceita esta responsabilidade que é imputada aos artistas na durabilidade das suas obras?

JS: Não. De maneira nenhuma. Não estou rigorosamente interessado. Se as obras desaparecerem, desapareceram. Estou-me nas tintas. Admito que o conservador não queira que as obras desapareçam e que a queira conservar, mas então o problema é dele. Porei sempre ao dispor de todos os conservadores (como já tenho feito) todas as informações que precisarem… amostras, por exemplo o… pediu-me amostras dos pigmentos e dos PVA, dei-lhes tudo, para as obras que eles têm minhas, para terem lá, para criarem um banco de dados. Não vou modificar um milímetro do meu trabalho a pensar na durabilidade. Vamos lá ver … se eu tiver dois papéis que são rigorosamente iguais e se um durar cem anos e outro durar cinco, então é logico que usarei o que dura cem anos. Mas, se um deles for ligeiramente mais branco e eu quiser o mais branco, pois então eu vou usar o mais branco.

AIP: Mas, para si "os artistas criam ou, trabalham para a imortalidade" …?

JS: Sim, mas …acho que sim. Acho que a única razão para a qual os artistas trabalham é a imortalidade. Acho que fundamentalmente é essa.

AIP: Qual a sua experiência prática com o envelhecimento e degradação das suas pinturas? Já atrás referiu o amarelecimento do PVA.

JS: Provavelmente é a única. E, ainda por cima, é um amarelecimento calculado, porque eu sei que isso vai acontecer. E depois é estável, amarelece de uma maneira e depois não amarelece mais. Mas, curiosamente materiais que me diziam "isto vai durar um mês, vai durar dois meses"…eu no início dos anos 80 trabalhava com papel de embrulhar bacalhau que é um papel

com um grau de acidez alucinante, com tintas *Sabu* que são abaixo do foleiro e as obras estão que parece que foram feitas hoje, quando foram feitas em 1980.

AIP: Portanto, não o preocupa que os pigmentos possam perder a cor, alterando-se não só a cor como a sua intensidade e se criem novos contrastes cromáticos? Preocupa-o que os aglutinantes possam vir a alterar-se, alterando por sua vez os valores cromáticos originais?

JS: Não, quer dizer se eu poder obviar a que isso aconteça pois eu obviarei…há uns quadros que eu agora estou a fazer e que não quero mesmo que amareleçam. O que estou a fazer é trabalhar com gesso acrílico, que em princípio não amarelecem. Ou seja, faço a base com PVA e pigmento branco para ficar com textura que eu quero e depois pinto por cima com gesso acrílico… É um artista americano, um dos pais da arte conceptual. Eu troquei uma obra com ele aqui há uns anos e a obra quando a recebi vinha toda "janada" tinha uma fotografia com bocados de tinta a sair escrevi-lhe e disse-lhe "isto está tudo lixado achas que mande retocar, que mande restaurar?". E ele disse-me que não queria mesmo (eu acho que isto é um grande ensinamento) porque não se deve pôr maquilhagem nas obras de arte. È como as pessoas. As pessoas envelhecem, as obras envelhecem. É como as velhas de Hollywood, de Beverly Hills que depois ficam todas de plástico, não é? As obras são como são. Envelhecem como envelhecem. Não ficam piores por causa disso. Ficam com ar do tempo, que também é importante.

AIP: Poderia descrever, caso existam, experiências negativas e positivas com processos de conservação e restauro das suas obras.

JS: Houve obras minhas que foram restauradas de facto. Mas, foram sempre bem restauradas. Não tenho assim nenhum caso em que me possa lembrar de uma experiência negativa.

AIP: Desejaria ser consultado relativamente ao estado de conservação e de medidas de preservação das suas obras?

JS: Não.

AIP: Gostaria de ser mantido à parte?

JS: Não. Bem aqui, não é uma questão de gostar ou, deixar de gostar. Se a determinada altura alguém achar que é importante entrar em contacto comigo para saber alguma coisa para restaurar uma obra minha eu estou disponível. Não me importaria de ser contactado.

Exibição/Preservação

AIP: Para si a arte "é uma prática física, quase, física porque eu faço objectos que podem ser vistos e nalguns casos tocados". Nesta perspectiva, seria a favor, ou contra, a colocação de alguma das suas obras (seja ela em papel, ou tela ou outra técnica) em caso de ser necessário para a sua preservação numa moldura envidraçada?

JS: Em caso de ser necessário não sou contra, porque ás vezes é mesmo importante, protege mesmo. Fundamentalmente essas pinturas em papel que eu fiz nos finais dos anos 80 eram para ser pregadas à parede. Mas, muitas foram vandalizadas. Pelo menos se estiverem dentro de uma caixa com vidro pelo menos escapam.

AIP: Apesar das margens nem sempre serem uma continuação perfeita da tinta da superfície, as suas pinturas não foram feitas para serem emolduradas, pois não?

JS: Não, de maneira nenhuma.

Autenticidade

AIP: Poderia descrever qual o papel dos assistentes das obras.

JS: Fundamentalmente, ajudam. Fazem quase sempre tudo aquilo que eu acho que qualquer pessoa pode fazer. Depois há aquilo que eu acho que só eu é que posso fazer. Por exemplo, eu estou a fazer um fundo branco, tenho uma série delas em que repito os fundos e que são mais ou menos iguais, digo "João, é assim…". Para que é que eu vou fazer uma coisa que é completamente mecânica? O resto faço eu.

AIP: Até que ponto é a "mão do artista" importante na produção das suas obras?

JS: Eu, por princípio e por postulado deveria de dizer que não é importante mas, acaba sempre necessariamente por ser. Porque por muito que eu diga a um assistente meu a maneira como deve desenhar uma coisa ele nunca a vai desenhar como eu desenharia. Eu agora estou a trabalhar com uma série de pinturas que são uma espécie de silhuetas a negro. O que eu faço…é eu desenho a silhueta toda. É um "trabalho de cão" estar a pintar tudo aquilo a preto. De modo que eu faço o "outline", a silhueta toda e ele depois preenche o preto por dentro. Mas, isso até uma criança pode fazer. Agora, a linha exterior que vai definir o espaço negro tenho de ser eu a fazê-la.

AIP: Sei que na instalação *Amazônia*, 1992, foi o seu assistente que desenhou os motivos…

JS: Aí foi o meu assistente a fazê-las. Mas, porque eu queria mesmo que fosse o meu assistente a fazer os desenhos. Porque não queria ser eu a fazê-lo.

AIP: Porquê?

JS: Porque eu queria que eles fossem autenticamente ingénuos. E eu nunca os poderia fazer autenticamente ingénuos, já não seriam autênticos. Ele (o meu assistente que era um brasileiro das roças) não escolheu o que fazia eu dizia-lhe "Faz isto" e ele fez aquilo que eu lhe disse para fazer mas, à maneira dele. Portanto, o conceito por trás daquilo fui eu que lho dei.

AIP: E na obra feita para a exposição *The House with the upstairs in it* na qual o seu filho desenhou uma parte da sua obra?

JS: Há várias, não é só uma. Não é desenhado pelo meu filho. Isto foi de um desenho que o meu filho fez. Fiz um slide do desenho dele projectei em cima do papel e pedi a um assistente meu que desenhou tal e qual. Pelo slide passou exactamente o desenho. Portanto, não é feito por mim, é baseado, de facto, numa coisa que o meu filho fez (que era um bebé nessa altura, devia ter para aí um ano). São vários em que se seguiu sempre o mesmo princípio, projectado, desenhado tal e qual. Eu não inventei nada. A metodologia era assim: aqui é um papel A4, o desenho era projectado e aqui já não havia desenho era só a luz do projector de slides e onde havia luz foi pintado de preto.

1.2. Entrevista 2: 16 de Junho de 2008

Participantes Julião Sarmento e Ana Isabel Pereira

No estúdio do artista (Centro Empresarial de Sintra-Estoril, n.5, Armazén B-8)

O objectivo da segunda entrevista foi o de clarificar algumas questões levantadas durante a entrevista resalizada em 2004. Além disso, a documentação fotográfica do atelier feita nesse ano mostrava tubos e frascos de tintas antigos que tinham uma importância histórica. Nomeadamente, frascos antigos da tinta portuguesa *Sabu* e da tubos de tinta britânicos produzidos pela *Rowney*. Ambas as marcas já não são produzidas portanto, era essencial registá-las e analisá-las. A entrevista começou com uma conversa com Sarmento sobre o aglutinante que o artista mais usa a cola branca *Vulcano V7*.

AIP: Actualmente a cola *Vulcano V7* foi substituída pela cola branca *Bizonte*…
JS: Sim, mas o único problema com a *V7* é que amarelecia e muito rapidamente.
AIP: Nós vamos fazer algumas experiências com diferentes pigmentos para perceber de que forma o pigmento pode estar a influenciar esse processo. Queremos ver se o branco de titânio e se o litopone 'protegem' ou, não o polímero. Vamos começar pelos brancos e negros visto que são as cores que acabou por usar mais.
JS: Isso seria muito bom. Nos dias que correm estou a fazer um truque. Porquê? Porque todas as pinturas que fiz e que eram brancas estão agora realmente amarelas.
AIP: Mesmo as que são recentes?
JS: Sim, vamos dizer…aquelas feitas por volta de 2000 já estão…laranjas. Neste momento estou a tentar fazer uma coisa…estou a experimentar a ver se consigo evitar isso porque me está a incomodar. Por um lado admito o facto de haver uma mudança de cor. Por outro lado irrita-me porque gostava que permanecessem brancas. Em vez de admitir que há uma mudança de cor preferia não ter de o admitir e que continuassem brancas. Portanto, o que estou a fazer agora é fazer os fundos exactamente como costumo fazer com o PVAc e branco de titânio ou branco de zinco depende…
AIP: Se está a usar o branco da *Cenógrafa é* litopone...
JS: E depois o que é que eu faço? Depois pinto com gesso acríçlico por cima.
AIP: Essa era uma das questões que tinha. Qual é marca de gesso acrílico que usa?
JS: Uso da *Winsor&Newton* ou *Talens*, usualmente da *Talens* porque é mais fácil de encontrar. O gesso acrílico não amarelece, pois não?
AIP: Supostamente os acrílicos são mais estáveis que os vinílicos Essa é uma das questões que estamos a tentar verificar. Neste ponto da investigação estou apenas a tentar descobrir que tintas de base vinilica podem ser encontradas no mercado. Existem as *Flashe* as da *Rowney* das quais o Julião tem alguns tubos…de facto ia perguntar se o Julião se consegue lembrar em que obras possa ter usado as tintas *Rowney*.
JS: Não, não me lembro.
AIP: E os pigmentos da *Cenógrafa*? Agora estão a vender outros é isso?
JS: Sim.
AIP: Nós tentámos comprar pigmentos da *Cenógrafa* mas, a *Favrel* já não tinha. A fábrica fechou e o stock residual acabou. Acabámos por encontrar algumas embalagens numa pequena loja de

materiais para artistas no centro da cidade. Tinham trazido do armazém nessa manhã. Felizmente ainda tinham uma embalagem de branco e uma embalagem de negro da *Cenógrafa*. Outra das questões que precisava de se clarificar é que na entrevista realizada em 2004 o Julião afirmou que nos anos 80 raramente usou tintas acrílicas, certo?

JS: Sim, é verdade.

AIP: Mas, as obras feitas em 81 e 82 estão todas classificadas como sendo acrílico…

JS: Ah, mas isso era feito com a tinta…como é que se chamavam…eram da *Casa Varela*…

AIP: As *Sabu*?

JS: Sim as *Sabu*, é isso.

AIP: Mas, as *Sabu* são à base de PVAc.

JS: São PVAc?

AIP: São sim.

JS: Porque eu perguntei-lhes e eles responderam que eram à base de acrílicos, de têmpera acrílica.

AIP: Exactamente como anunciam nos catálogos.

JS: Não tenho a certeza se lhe disse na entrevista anterior mas, eu tinha uma espécie de regra. Eu usava tudo o que eu conseguisse encontrar e que fosse mais barato. Isto é absolutamente verdade porque, tudo começou por uma questão de necessidade. Eu não tinha dinheiro. E é engraçado como a certa altura se falou e escreveu tanto sobre o facto de eu usar papel de embrulhar, o quale u comecei a usar quando comecei a pintar. Além de gostar deste tipo de papel era muito barato. Eu não tinha um cêntimo na altura, não tinha dinheiro nenhum. Portanto, usava as tintas *Sabu* que eram baratas, aquele tuipo de papel que era super barato e o que aconteceu? Então comecei a usar um certo tipo e material. Dava-me gozo usar alguns materiasi em particular. Nalguns casos mesmo depois de começar a ganhar algum dinheiro não mudei porque gostava de usar aqueles materias porque, me acostumei com eles. Mas, a única razão pela qual tudo começou foi a de que não tinha dinheiro e estes eram os materiais mais baratos que conseguia encontrar no mercado.

AIP: Os quais não são necessariamente os de pior qualidade. Portanto, para além do amarelecimenrto viu algum outro tipo de alteração ocorrer nas suas pinturas? Fissuras?...Ou, são apenas danos devido à manipulação das obras?

JS: Não, a tinta não fissura.

AIP: Existem algumas pinturas no catálogo *Flashback* [59], que têm um fundo verde que julgo que foram feitas quando o Julião esteve na Amazónia. Nas fotografias Vê-se o que parecem ser fissuras nas camadas pictóricas.

JS: Não sei o que será porque não tenho nenhuma dessas pinturas comigo.

AIP: Há uma em exposição no Centro Cultural de Belém.

JS: Sim, há uma no CCB. Outras estão no Brasil e outras em colecções privadas. De qualquer das maneiras lembro-me que nessa altura foi muito diferente. O PVAc que usei naquela altura era brasileiro e fissurava muito mais do que o que eu usava aqui. Este daqui é mais elástico.

AIP: Lembra-se da marca do que usou lá?

JS: Não tenho a cereza se alguma vez soube. Nem tenho a certeza se existia uma marca. Mas, era seguramente muito mais rígido do que o daqui. A *Bizonte* é muito mais flexível.
AIP: Então ainda usa a *Bizonte* com o pigmento em pó?
JS: Sim, compro sacos que são muito mais baratos.
AIP: O Julião refere frequentemente em 2004 o branco de titânio. No entanto o branco da *Cenógrafa* é litopone…
JS: Bem…eles diziam que era feito à base de branco de titânio. Tal como diziam que as *Sabu* eram acrilícos.
AIP: Nas fotografias do atelier podem ver-se várias latas de tinta industrial para revestimento de paredes da *Robiallac* e da *Sotinco*. Lembra-se em que pinturas essas tintas foram usadas?
JS: Sim sei. São recentes. São sobre papel. São de uma série chamada *What makes a writer great*[33]. Foi tudo feito com esses esmaltes aquosos. Nunca os usei sobre tela só sobre papel.

1.3. Workshop no DCR – 3 de Maio de 2010

Participantes Julião Sarmento, Romeu Gonçalves, Maria João Melo, Ana Isabel Pereira, Joana Lia Ferreira, Leslie Carlyle, Estudantes do Mestrado de Conservação e Restauro da disciplina de História e Técnicas de Reprodução Artística Lectures (ano académico de 2010/2011); Jorge Imaginário (produção de vídeo)
Teve lugar no departamento de Conservação e Restauro, Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa, Campus de Caparica.
Em Maio de 2010 Sarmento foi convidado para realizer um workshop para o curso de Conservção de Restauro na disciplina de História e Técnicas de Produção Artística. O convite tinha o prósito de o próprio artista mostrar aos alunos de que modo a pintura *Frozen Leopard* tinha sido feita para que pudessem realizer uma reprodução seguindo as intruções do artista. A transcrição seguinte foi feita a partir do filme que foi realizado durante o workshop.

Julião Sarmento: Então vamos lá a ver…agora que eu sei que isto é para reproduzir o *Frozen Leopard*...vamos ver. Devo dizer que acho que é muito boa ideia fazer isto Então é assim, eu sou muito pouco disciplinado na tecnologia. Eu acho que é muito importante que se faça isto porque, mesmo a nível internacional, tenho visto grandes asneiras feitas em relação ao meu trabalho e ideias completamente erradas sobre o modo como trabalho. É usual ver a técnica descrita como sendo óleo sobre papel. Eu devo dizer que gosto imenso de óleo. Não tenho nada contra o óleo. Eu trabalhei com óleo na Escola quando estava a tirar o curso. Mas, devo dizer que pintei dois quadros a óleo na minha vida. Dois!
Maria João Melo: Mas, gosta muito do óleo?
JS: Mas, repare que também gosto de muitas outras coisas que não uso porque acho que não são apropriadas. E o óleo não é apropriado para o que eu quero. Eu sou muito mais rápido que o óleo.

[33] A série *What makes a writer great* foi feita entre 2000 e 2001.

MJM: E ainda por cima seca mal. Vai secando e vai estragando.
JS: Portanto, ideias básicas que é preciso saber sobre o meu trabalho. Desde o ínicio que adequo os materiais aquilo que quero fazer. Normalmente. Mas, muitas outras vezes adequo o que quero fazer aos materiais que tenho. Eu sempre fui bastante inventivo a nível dos materiais. Apesar de não ter uma costela judaica ou escocesa parece que tenho porque sou muito forreta. Primeiro era forreta porque não tinha muito dinheiro. Agora já posso gastar mais dinheiro continuo forreta porque não acho que valha a pena gastar mais. Também assisti a grandes dissertações e coisas escritas sobre porque uso este determinado tipo de papel ou, outro, este pigmento ou esta cola. É muito simples eu começei a usar a cola e o pigmento em pó porque era muito mais barato que comprar acrilícos. Depois pensei que aquilo dava uns efeitos que eu não conseguo com os acrílicos. E depois consigo…sei lá… superficies de 10m por 2m ao mesmo preço que uma superfície de 70 por 70 feita em acrilico. É economia pura.
MJM: Nós estamos a descobrir que estas formulações antigas de PVAc são provavelmente mais estáveis que os acrílicos. Portanto, seriam mais baratas, mais estáveis e mais adequadas à técnica.
JS: Já no início dos anos 80 eu pintava em papel de embrulhar bacalhau, um papel castanho acizentado…não conheço outro nome…não é papel de embrulho…parece papel reciclado mas é mais grosso. E porque é que comecei a trabalhar com este papel? Porque eu comprava resmas deste papel de embrulhar bacalhau com cerca de quatrocentas ou quinhentas folhas de 1,20m, 186cmx102cm. E isso custava-me…não sei…cerca de duzentas dessas folhas eram o preço de uma folha de papel da Fabriano. É economia. Portanto, tudo isto…ou seja eu adequei, fui adequando o meu trabalho aos materiais que utilizava em vez de ser ao contrário. Eu tenho um grande amigo, que vocês provavelmente conhecem que é um artista suiço-americano que vive em Portugal e que se chama Michael Biberstein e que é exactamente o oposto de mim. É giro fazer esta dictomia. Porque ele queria fazer uma pintura deste tamanho [Sarmento 'desenha' com as suas mãos um pequeno quadrado] e gastava toneladas de dinheiro. Comprava pincéis de pêlo de marta de não sei quantos números…ele comprava os materiais mais caros que encontrava. Eu era exactamente o contrário.Eu usava um pincel que era o mais barato que comprava na *Casa Varela*, aquilo comprava-se às dúzias. Que eram pincéis que mais ninguém queria, que iam para o lixo e eles reciclavam, que eram feitos para aí de pêlo de cavalo com um pedaço de lata à volta e usava esse tipo de material. Porque me dava gozo usar isso e depois tornou-se natural dar-me gozo usar esse tipo de material.
MJM: Da *Casa Varela*?
JS: Eu utilizava tudo da *Casa Varela* porque tudo me saía mais barato lá. Não é que eu tivesse uma paixão pela *Casa Varela*. Existe uma razão muito simples. Eu quando entrei para a Escola Superior de Belas Artes de Lisboa um dos colegas do meu curso…bem eu primeiro entrei para Pintura e depois fui para Arquitectura….quando entrei para o primeiro ano de Arquitectura um dos meus colegas de curso era um tipo chamado António Varela e então o Mário Varela era o dono da Casa Varela. Ele fazia-me preços mais baratos em tudo portanto, eu comecei a comprar tudo na Casa Varela. Todos os meus materias eram comprados na *Casa Varela*. E ainda hoje é assim.

MJM: Por acaso não sabe se o Rodrigo, o PVAc...
JS: Eu devo dizer-lhe que há coisas que o Rodrigo era bastante pouco elucidativo em relação a isso…Nós erámos uma espécie de escravos que eram pagos à hora. .
MJM: Pensei que ele vos mostrava tudo…
JS: Não, ele aparecia lá com os materiais e nenhum de nós fazia a menor ideia onde é que el comprava as coisas. E duvido que o Rodrigo fosse comprar à *Casa Varela*. O Rodrigo era pior que eu. O Rodrigo ia daqui a Badajoz para comprar cigarros se fossem mais baratos lá.
MJM: Bem, o Mário Varela disse-nos que ele ia lá.
JS: Se calhar ia. Eu não estou a dizer que ele não fosse. Eu estou a dizer que eu não sei. Bem…pronto é esta a razão porque é que compro as coisas na *Casa Varela*. Quando eu recomecei a pintar…Ah! E enquanto restauradoras há três períodos fundamentais do meu trabalho que devem ficar a conhecer. Até 1974 eu pintei a acrílico sobre tela. Eu mandava fazer s telas ou, comprava telas já feitas, de linho normal. Eu mandava-as fazer na *Casa Ferreira*. Mas, nessa altura a *Corbel* abriu na Praça do Camões. E eu e o Fernando Calhau descobrimos que a abriu a *Corbel* e então fomos lá e eles viram dois jovens artistas e começaram a fazer preços mais baratos portanto, começámos a ir á *Corbel*. Então começámos a mandar fazer as telas na *Corbel*. Aquelas normais e correntes de linho que já estavam preparadas e depois pintávamos a acrílico sobre tela. Até 1974 todas as minhas pinturas, exceptuando uma ou duas que eram a óleo, são a acrilico sobre tela.
MJM: E a marca?
JS: E acrílicos *Talens*. Nós viviamos o sonho de pintar com a *Aquatec* que era com o que os Americanos pintavam mas, aqui em Portugal não havia. Davámos uma base muitas vezes por cima. Muito frequentemente por cima da preparação da tela dava uma ou, duas camadas de gesso acrílico, da *Talens* também. E depois era pintura acrílica da *Talens* sobre tela. Tudoo que é obras até 1974, exceptuando algumas….de cerca de 1969…fins dos anos 60…Eu devo dizer que no futuro vocês encontrarão muito poucas obras minhas dessa altura. Porque, infelizmente, e vocês talvez já saibam disto, houve uma série de acidentes na minha vida que me fizeram perder uma grande parte do meu trabalho. Um deles foi…
MJM: O incêndio em Belém.?
JS: Sim, mas aí em Belém foi sobretudo trabalhos em fotografia, trabalhos feitos nos anos 70. Perdi filmes, arquivos, fotografias, negativos. Trabalho fotográfico dos anos 70 dos quais não resta nada. Nem sequer os originais. Arderam os negativos e arderam os positivos. Ardeu tudo. Portanto….mas eu vivi entre 1967 e 1974 na Rua Nova do Almada, vivia no Chiado por cima da Casa Batalha e eu tinha lá muitas coisas. Vivi lá com a minha segunda mulher mas, depois separei-me e como costume ela ficou com grande parte das minhas coisas. Eu tinha muitas coisas lá e muitas pinturas dos anos 60, pinturas dos anos 60 que se não arderam no incêndio de Belém arderam no incêndio do Chiado. Mas, ainda há duas ou, três dessas pinturas. São excepções…que eu fiz no final dos anos 60, cerca de 68,69. Nessa altura eu fazia uma grade em pinho que era forrada por um suporte rígido, seria forrada por uma placa de platex. Ou seja, era uma tela dura. Em vez de ser uma tela era platex. E eu pintava sobre o platex.

Joana Lia Ferreira: Só por curiosidade de que lado do platex é que pintava?
JS: No lado liso. E nessa altura usava normalmente…vamos ver se me consigo lembrar do nome da tinta…usava tinta de pintar paredes…
JL: *Robiallac*?
JS: Não! Isso era muito caro.
MJM: *Dyrup*?
JS: Não
JL: Havia uma marca portuguesa que se chamava *Soberana*.
JS: Não, era ainda mais barato que isso. Ninguém conhecia. Foi uma tinta que eu consegui descobrir numa drogaria do Porto. Se eu conseguir descobrir entretanto eu aviso. Bem…e então…eu pintava com essa tinta…tudo o que era baço eu pintava com essa tinta. Eu pintava muitas vezes com baço e brilhante. O que era brilhante eu pintava com Robiallac porque era uma tinta com um bocadinho de melhor qualidade. Porque a outra era transparente demais.
MJM: E isso foi quando? Qual foi o período?
JS: Entre 62-69. Mas, só restam para aí duas ou três obras dessa altura. Depois voltei ao acrilíco sobre tela. Ou seja, este foi um período de telas duras e depois voltei a usar telas normais, telas de linho. Em 1974 num acto desesperado de jovem artista larguei…mas, abandonei competamente entre 1974…e isto é rigorosamente verdade…há um período de sobreposição em que fiz as duas coisas, fotografia, pintura e desenhos…mas entre o finais de 1974 e 1981 não fiz uma pintura, não fiz um desenho. Fiz meia dúzia de esboços, projectos para instalações. Mas, são trabalhos pessoais, não funcionam como obras, certo? Há bocado referi os falsificadores porque surgiram algumas pinturas datadas de 1978 e isso não é possível, não existe nenhuma. Bom, portanto nesta altura eu trabalhei única e exclusivamente com fotografia, com vídeo com som, com filme Super8, com instalações…Um trabalho que tem a ver com uma reprodução mecânica. Em 1981 com o triunfo de Hockney voltou a febre da pintura e aí lá vou eu a casa do meu amigo Mário Varela e lá fiz um esquema com ele. E aí é que começa esta aventura que vocês querem aprender a reproduzir. Naquela altura já havia um certo gasto da arte conceptual ou melhor da arte pós-conceptual porque não houve arte conceptual em Portugal…as pessoas em termos genéricos voltaram a uma espécie de 'estado-zero' e as coisas tinham de se impôr por si prórias, pela sua própria dimensão. As pessoas pintavam coisas enormes. E então entre 1981 e 1983…se também aparecer alguma tela é falsa porque eu nunca trabalhei com tela, trabalhei sempre, sempre em papel. No tal papel de embrulhar bacalhau. Em 1983 fiz algumas tentativas um bocado goradas de comprar telas mas, não estava preparado para isso ou, senti isso porque era demasiado caro. Portanto, usava pano cru ou pano de lençol e ainda tenho algumas coisas pintadas em pano crú. Agarrava naquilo, esticava e pintava com várias camadas de *Sabu* que era o mais barato. Cheguei à conclusão que a *Sabu* aquilo rendia, aquilo era uma espécie de tempera. Eu comprava, eu tinha toneladas de frascos de *Sabu* e isso…
JL: Era super concentrada, podia-se diluir…
JS: Era uma maravilha, podia usá-la para qualquer coisa, podia diluir…mas, fissurava…
MJM: Fissurava?

JS: Claro que sim! Fissurava e de que maneira. Uma camada grossa de *Sabu* bastante concentrada…A *Casa Varela* não é propriamente o suprassumo do requinte e eu não sei como é que eles faziam aquilo mas, mas muitas vezes eu abria uma lata de *Sabu* e a tinta tinha uma certa consistência e na semana seguinte a mesma tinta, com a mesma cor e a mesma referência…para além de não ter a mesma cor tinha outra consistência. Ou era mais densa ou, era mais espessa…
JL: Mas, de outro frasco?
JS: De outro frasco, obviamente. Quer dizer não era pacífico você dizer assim, era um cor-de-rosa escuro mas, não não era igual. Nunca era igual.
MJM: Mas, eles eram cuidadosos na escolha do aglutinante e os pigmentos também eram de boa qualidade.
JL: Sim, mas a formulação complete da tinta…
MJM: Sim, a mistura era manual. Mas, portanto a matéria base era boa.
JS: Provavelmente era, eu acredito nisso.
MJM: Mas, com certeza que aplicar uma camada de tinta muito espessa desde que tenha cargas, pode-se ir aplicando pacientemente camada a camama ou, se fôr como eu imagino que o Sarmento aplique…
JS: Espere lá, aquilo era pintado com pincéis…bem, tudo isto para chegar ao *Frozen Leopard* que é o que nos trouxe aqui. Em 1985 dá-se um outro shifting na maneira como trabalho. Foi quando comecei a trabalhar com este PVAc, com a *Vulcano V7*.Comecei a pensar que de facto tudo é um pigmento e comecei a usar muitos tipos de pigmentos diferentes. Se eu agarrar em vocês todas e vos meter na cola Vulcano e usar assim é um pigmento. As pessoas são pigmentos. Pigmento é tudo o que se possa agarrar com o ligante.
MJM: Bem, mas isso não seria uma cor muito gira, certo?
JS: Sim, mas está a ver o meu ponto de vista? Quarenta cadeiras arruinadas é pigmento. Pigmento é isso…são partículas que podem ser misturadas com o ligante. E então comecei a pensar nisso e cheguei à conclusão que se comprasse…porque eu queria fazer pinturas muito grandes…e nessa altura eu procurei pela Rua da Conceição onde havia umas casas de tecidos…e cheguei à conclusão que em Portugal não havia pano cru. Porque eu tela? Nem pensar. Porque honestamente não tinah dinheiro para comprar tela. Conseguia comprar lona, pano crú. Não havia em Portugal e acredito que continua a não existir…não havia pano no tamanho que eu queria. Vamos dizer que a largura máxima que eu encontrava desse pano crú em todo o território nacional era 1,50m. E creio que continua a ser. E eu queria que fosse mais largo. De modo que comecei, e na altura eu estava a trabalhar em Madrid, comecei a mandar vir pano de Espanha. Cheguei à conclusão, curiosamente, que essa tela para além de ser de melhor qualidade do que a que eu comprava em Portugal…comprava um rolo de 2,15m de largura e saía-me mais barato que comprar 5m de tela com 1,50m em Portugal. Não percebo como é que eles conseguiam fazer essas contas mas, lá era realmente mais barato. Eu hoje em dia continuo a mandar a tela de Espanha.
MJM: Mas, é um material feito em Espanha?

JS: Sei lá. Não sei onde é feito. Só sei é que vindo de lá…eu compro tela a rolo com 2,15m de largo…compro esse pano a rolo e agora gosto de trabalhar com isso. É muito mais barato.
JL: Só uma questão, não a lava?
JS: Sim…não, não lavo. Molho-o. Já vão ver como é que eu faço.
MJM: E a firma de Espanho manteve-se sempre a mesma?
JS: Não faço ideia.
MJM: Quem é que encomenda a tela?
JS: É o Romeu.
MJM: Ah…então depois perguntamo-lhes a ele?
JS: Não, a gente encomenda às diversas galerias com quem trabalha. Nós dizemos "arranja aí um rolo deste tamanho" e eles arranjam.
MJM: Mas, vem de Espanha sempre?
JS: Sim, vem sempre de Espanha…umas vezes de Barcelona, outras vezes de Madrid
JL: Talvez haja uma etiqueta que diga de aonde...
Romeu: Geralmente não tem uma etiqueta.
MJM: Ok, podemos tentar perceber isso mais tarde.
JS: Mas, repare que cheguei à conclusão que deve ser muito fácil arranjar essa tela porque já vem desde essa altura e mando vir desde Barcelona à Galiza. É sempre diferente, tem espessuras diferentes ou cor diferente mas tem sempre 2,15m e custa sempre barata, que é o que é fundamental. Aliás eu trouxe aqui uns restos que vos ofereço. Tenho telas dessa altura para aí de 85. Até trouxe uma Portuguesa para verem a diferença…Bom…Onde é que eu ia?...Eu comecei a trabalhar com isto e a explorar…
JL: Á bocadinho estavámos a falar do pigmento e de que começou a pensar que tudo é um pigmento.
JS: Exactamente, e então eu comecei a pensar no que podia encontrar na *Casa Varela*. E isso chamava-se...como é que era?...de Serigrafia.
AIP: Da *Cenógrafa*?
JS: Exactamente. Durante todos os anos 80 era o que eu usava.
MJM: Da *Cenógrafa*?
JS: Pigmentos de cenografia. Até tenho alguns aqui desse tempo, os autênticos e legítimos. São de quando usava essas cores. E as embalagens eram sempre iguais. Nessa altura fazia uma coisa que já não faço hoje em dia porque comecei a ter um bocadinho mais de cuidado comigo. Eu nessa altura trabalhava com as mãos. Fazia tudo com as minhas próprias mãos, misturava as tintas com as minhas próprias mãos. Mas, depois a minha pele começou a ficar toda gretada e depois começei a usar luvas e depois começei a usar asistentes. Ah!…a partir de 1990…Eu sempre tive uma paleta de cores muito reduzida primeiro porque os pigmentos de Cenografia não tinham assim tantas cores como isso. Depois só usava as cores que gostava mais ou menos o que limitou ainda mais a minha paleta e depois a partir de 1990 cortei mesmo e só trabalhava com tinta branca ou preta ou, misturando o branco com o preto. O facto de trabalhar com a cola *Vulcano* ou a *Bizonte*, aliás como com qualquer outro poliacetato de vinil, como sabem, tem um

problema…é que fica amarelo. Os quadros são branquinhos, de um branco imaculado quando acabados de fazer e depois ficam amarelas.

MJM: Mas, as pinturas do Rodrigo não ficaram amarelas. Pelo menos a Joana fez medidas…

JS: Mas, a quantidade de PVAc nessas camadas é muito reduzidissima. Nas minhas eu uso um boião destes…eu normalmente…a maneira como eu trabalhava era…as minhas misturas eram um boião destes e eram 2kilos de pigmento. Depende mas por média seriam dois pacotes de pigmento para 5 litros de cola. O que é que acontece? É que muitos quadros brancos que naquela altura eram branquíssimos e hoje em dia estão amarelos. Têm superfícies amareladas e outras brancas. Onde há mais PVAc está mais amarelo. Mas, não me incomoda, eu sei que amarelece.

JL: E as pinturas do Rodrigo têm titânio.

JS: E têm imensa água.

MJM: Mas, mesmo assim têm bastante ligante, tanto ligante como as tintas normais.

JL: E não têm cargas.

MJM: mas, não estão a ficar demasiado amarelas…? É só nos sitios onde têm muito aglutinante?

JS: Algumas estão a ficar. Tenho alguns que estão amarelos mesmo!

AIP: A Belém é o caso que me chamou mais atenção. Mas, também está exposta num sítio público, perto de um café onde é permitido fumar.

JS: Por exemplo, tenho uma amiga minha que fuma imenso e aquilo está a ficar mesmo ocre.

MJM: Se desejar isso seria algo que a Ana Isabel poderia fazer no seu doutoramento, testar alguns aditivos que poderia pôr no PVAc para evitar que amareleça.

JS: Ultimamente, não tenho querido que amareleçam.

MJM: Este PVAc pensamos que está a envelhecer bem porque as novas formulações são péssimas, são péssimas para os artistas.

JS: É evidente que todos os brancos ficam amarelos, certo? Acabam por ficar, ou não?

MJM: têm mais tendência para mostrar isso. Mas, olhe que os brancos do Joaquim Rodrigo que têm trinta anos estão quase tão brancos como as reproduções da Joana.

JL: Têm quarenta anos. Sim, a maioria. No entanto há um caso em que amareleceu.

MJM: Mas, os brancos são feitos com branco de titânio.

JL: Sim, é que o branco de titânio é muito branco. Mesmo que o polímero esteja com alguma tendência para amarelecer como a quantidade de pigmento é elevada…

JS: E o branco de *Cenógrafa* é feito de quê? É zinco?

AIP: É litopone. É bário e zinco.

JS: Isto quando se olha para a arte de uma maneira tão técnica…é bom que vocês existam mas, se começo a pensar, se começamos a pensar demasiado nisto…não faço mais nada…

Reprodução de uma pintura dos anos 80

JS: Primeiro molhava a tela e depois tirava as bolhas de ar. Usava sempre um plástico por baixo. É por isso que todas as minhas telas têm uma espécie de 'rios' na parte de trás que são marcas do plástico que está por baixo. No entanto, tudo isto era pensado. Há várias maneiras…eu vou fazer como nos anos 80.

Leslie Carlyle: Se tiver um grande pedaço de tela como é que molhava?

JS: Bem depende, usualmente deitava água em cima e depois espalhava com as minhas mãos. Ou, usava um bocado de madeira.
MJM: E usa a cola assim, directamente sem diluição?
JS: Sim, completamente.
MJM: Mas, parece que tem tanto pigmento.
JS: Agora…tudo isto variava consoante a espessura que queria da tinta. É evidente. Se eu quissesse super espesso fazia como estou a fazer agora. Se quissesse que ficasse mais liquida pois misturava-lhe mais água. Ou, normalmente, o que eu fazia também díluia a cola e misturava-lhe cola super diluída. Havia muitas maneiras de fazer isto. Dependia do que eu queria. Às vezes queria uma superfície inteiramente diferente e despejava água sobre isso e isso dava-me uma superfície completamente diferente. Outras vezes subia a um escadote e pingava água, gota a gota e isso fazia crateras, pequenas crateras na tinta. Mas, têm então aqui a típica dos anos 80. Não fundo não tem nada mais ou menos simples. Muitas vezes se eu queria ser mais engenhoso agarrava em terra, ia ao jardim e agarrava em alguma terra…
MJM: E peneirava?
JS: Qual peneirava. Atirava para aqui para cima e misturava tudo. Dependia daquilo que eu queria. Se eu quissesse peneirar, peneirava. Eu tinha um jardim grande e muitas vezes muitos destes quadros dos anos 80 eram feitos no jardim, eram feitas em cima da terra. E isto era molhado com a mangueira do jardim.
MJM: Mas, é verdade que a textura é uma coisa completamente característica em todas as suas obras?
JS: É e a textura era conseguida através da tinta. Mas, com as telas brancas, as chamadas Pinturas Brancas o esquema já é um bocadinho diferente.
MJM: Isso depois fica a secar assim?
JS: Sim, agora deixo a secar. A minha produção no Verão era sempre maios que no Inverno.
MJM: Não usava um secador?
JS: Não, eu nunca usava um secador. Isso dá muito trabalho. É deixar a natureza tratar das coisas. Depois de secar estava na altura de desenhar sobre aquilo já seco. Muitas vezes quando as obras são caraterizadas eu dizia que era técnica mista sobre tela porque tinham tanta tralha.
MJM: E fazia-as sempre no chão?
JS: Sempre.
MJM: E podía-nos só dizer se costuma desenhar verticalmente ou, também no chão, ou se depende?
JS: Dependia. Dependia das situações. Normalmente, normalmente é feito na vertical. Normalmente…mas, como em tudo na vida eu não tenho regras. Sou completamente destituido de regras. Não quer dizer que de vez em quando não faça uma na horizontal. Isto [os fundos] eram sempre feitos na horizonta por razões óbvias. E muitas vezes depois isto secava e fazia pinturas sobre isto com *Sabu* claro. Às vezes com *Sabu*, às vezes com tinta feita disto mas mais diluida. Umas vezes eram na horizontal outras vezes eram na vertical.
MJM: E a grade? Esticava antes de desenhar?

JS: Colocar na grade é a última coisa a ser feita. É a última coisa.
Student: A tela encolhe quando seca?
JS: Claro que encolhe e encolhe bastante. Por isso é que a grade é sempre a última coisa ser feita. Só depois de estar tudo pintado e sequinho é que podia saber o tamanho.
Estas Pinturas Brancas são trabalhadas de muitas maneiras consoante a superfície…a superfície varia…depende daquilo que quero. O que se passa é que tudo depende daquilo que eu quero. Há alturas em que me apetece que a superfície fique muito uniforme e faço de uma certa maneira. Mas, se patecer que a superfície não fique tão uniforme faço de outra. Se me patecer que a superfície tenha uma certa textura faço de outra…como já percebeu. Usando sempre pigmento, ligante e água. A maneira como espalho é que é diferente. Eu tenho um balde e uma daquelas misturadoras industriais. Deito lá para dentro a cola, deito o pigmento e misturo. Muitas vezes até ficar completamente homogéneo, ou seja uma pasta completamente homogénea e depois…E depois como vocês sabem, tudo depende do que eu quero. Há uma maneira de chegar lá mas, os resultados é que são todos diferentes. Muitas das vezes as telas têm umas superfícies em que quase se consegue ver a tela. Aí o que é? Pode ser feito de duas maneiras. Ou a tela estava super molhada, completamente encharcada, com piscinas de água. E eu deito a tinta lá para cima e nas áreas em que há muita água a tinta vai ficar mais díluida. Por isso quando seca pode-se ver a tela…Eu posso pegar no pigmento e misturá-lo pouco e a tinta fica cheia de grumos de pigmento.
MJM: Ah, então também controla aí?
JS: Sim, controlo aí….Ou posso querer que ela fique super batida então misturo tudo até ela ficar super cremosa. Aí eu controlo logo como é que vai ficar o resultado final. Eu fazendo as minhas tintas desta maneira, eu controlo tudo na tinta que quero. E são sempre diferentes por isso é que é difícil para mim explicar isto tudo.Umas vezes são mais liquidas, outras vezes são mais pastosas, às vezes é mais homogénea.
MJM: E no *Frozen Leopard*?
JS: No *Leopard*…a parte de baixo branca é feita com esse pigmento branco de cenografia. A parte de cima é feita com um pigmento que eu comprei em Marrocos, em Maraquexe. Comprado na rua.
Julião Sarmento a desenhar
Infelizmente não existia uma reprodução com uma textura trabalhada para que Sarmento exemplificasse como é que fazia os desenhos. Um pedaço de platex no qual tinha sido aplicado uma camada de branco de titânio com PVAc foi usado para a demonstração.
MJM: Então usava lápis?
JS: Não, com grafite, sim…mas era com pau de grafite.
AIP: Nós temos. Perefre que sejam mais macias ou…
JS: Macias, dessas que são macias e borram imenso.
MJM: E a grafite também comprava na Casa Varela?
JS: Não, a grafite era onde arranjava.
MJM: Mas, não comprava os materiais todos na *Casa Varela*? Também depende?

JS: Sim, a grafite seguramente. Ora bem, se vocês agora chegarem aqui vão vendo que aqui ao lado vão aparecendo estes fantasmas que costumam aparecer. São porquê? Eles aparecem naturalmente e resultam da minha mão ficar suja com o pó da grafite. Se eu desenhar outra forma aqui deste lado vocês vão ver o fantasma da árvore anterior.

MJM: E deixa ficar ou, remove-os com um pincel?

JS: Não, não, faz parte do processo.

AIP: E depois aplica alguma coisa sobre o desenho como um fixativo?

JS: Agora fixativo. Naquele tempo laca de cabelo *Elmut Satin*.

AIP: Mas, as pinturas ficavam a cheirar a cabeleireiro…

JS: Sim, ficavam a cheirar a cabeleireiro. E o problema era esse. Mas, era mais barato. Era o mais barato que comprava no Continente.

MJM: Mas era só sobre o desenho mesmo?

JS: Sim, a laca é um fixativo.

É claro que quando vocês estão a desenhar sobre uma superfície super texturada da tela há muito mais pó e o traço não fica tão regular. É completamente diferente do que está a acontecer aqui, não é?

A terceira fase do workshop foi dedicada à realização do fundo branco que se encontra na pintura Frozen Leopard. Este deverá ser o método habitual usado nas pinturas dos anos 90. Sarmento já havia colocado a cola branca Bizonte num outro balde de plástico e estava pronto para adicionar o pigmento em pó e iniciar a sua explicação.

JS: Ok…aqui é que reside a alma do artista! E há uma coisa que é muito importante que é a mistura, as proporções. Depende daquilo que eu quero. As proporções entre o pigmento e a cola não são sempre iguais. E eu fazia cola diluída em água.

Julião misturou a cola e o pigmento e depois adicionou alguma água. Entretanto, o seu assistente Romeu preparou a tela como haviam preparado antes. Mergulhou-a num balde com água e esticou-a com as mãos sobre o plástico que cobria o chão.

JS: De um modo geral eu não uso água nesta altura. Eu fazia outra coisa. Se eu fizesse exactamente como fazia naquela altura fazia de outra maneira. Para fazer rigororosamente como eu fazia naquela altura…A água é misturada lentamente. Isto é como cozinhar. Está bom quando parece chantilly.

MJM: E fez algumas experiências? Assim para ver como é que saíam os efeitos em telas mais pequeninas?

JS: Às vezes claro.

MJM: Então essa foi a textura que gostou?

JS: Que eu gostei…? Mas, para aqui acho que é o que vocês querem. Para reproduzir o *Frozen Leopard* era qualquer coisa deste género. Agora vou-vos pedir que se afastem. Romeu pode ir lá fora e trazer-me alguma terra?

MJM: Areia nós temos.

JS: Não, eu não quero areia. Eu quero terra. Vocês querem o *Frozen Leopard* não é? A vantagem destes processos é que cada coisa dá direito a uma experiência diferente.

MJM: E a terra começou a usar nestas pinturas brancas por algum motive em especial?
JS: Ás vezes olhava para aquilo e pareciam demasiados brancas…chateava-me.
MJM: Mas, com terra?
JS: Porque estava mesmo ali á mão de semear.
Nesta altura Romeu trazia alguma terra apanhada lá fora e colocou-a num balde com água. Sarmento com a mão salpicou esta mistura sobre superfície da reprodução.
JS: Pronto…o *Frozen Leopard*. Está feito. Agora é só secar. Vamos lá a ver, há coisas que eu nunca faço na vida real e acabei por fazer aqui para a demonstração. Por exemplo, vocês aqui …é visível a passagem dos dedos e da mão. Na vida real nunca deixo que isso aconteça. Estou ali meia hora até disfarçar.
MJM: Mas, como é que disfarçava, com as mãos?
JS: Sim, nesta altura…eu lembro-me muito bem do *Frozen Leopard* foi tudo feitinho à mão.
JL: Mas, quando uma tela tem três metros e dois como é que chega ao meio?
JS: Eu começo…eu ponho-me em cima da tela e começo numa ponta e depois vou avançando até à outra.
Student: Tem problemas com a secagem?
JS: Não, porque isto vai estar seco…não sei qual é o ambiente aqui…Mas, com este tempo e com esta temperatura, amanhã a esta hora já está seco. A secagem é rápida mas, não é assim tão rápida.
MJM: Então, a tela seca e costuma pô-lo logo na moldura…na grade?
JS: Não, a grade é a última coisa a ser feita.
Student: Mas, então como é que o desenho é feito com a tela na vertical se a última coisa a ser feita é esticar a tela na grade?
JS: Porque eu pegava na tela e agrafava- à parede. Mas, outras vezes também faço no chão, depende. Também é importante que saibam que nos anos 80…Eu só engradei telas até ter dinheiro para pagar a alguém que as agrafasse por mim. O meu primeiro assistente, o único trabalho que tinha (e por acaso era uma assistente) era engradar as telas, nada mais. Porque ao fim de engradar para aí mais de 500 telas já estava farto. Hoje em dia é aqui o Romeu que me engrada as telas.
MJM: Então, e para além da terra há mais alguma coisa que faça estes efeitos nestas pinturas brancas?
JS: Normalmente é o que está mais à mão. Já fiz com muitas coisas mas, depende. Mas, quando digo depende, depende das circunstâncias, depende da ocasião. Isto é porque quer que vocês percebam uma coisa e que é fundamental. E se vocês pensarem no meu trabalho nestes termos é fácil de lá chegar. Eu sou super permissivo a nível dos materiais que uso. Para mim não há tabus. Portanto, se eu achar a determinada altura que meto coisas de fita-cola ali, eu meto coisas de fita-cola ali.
MJM: E depois não aplica qualquer revestimento? È só o desenho fixado com a tal laca?
JS: Sim, e nada mais.

AIP: Acerca de pintura *Salto*, de 1985-86, papel colado sobre tela. Estamos a ter dificuldade na identificação da cola e a tinta parece impregnada por uma substância a qual temos dificuldade em identificar. Lembra-se que tipo de cola foi usada para colar o papel à tela?

JS: Quando esta pintura foi feita não havia nenhuma intenção de colar o papel a outro suporte. Deve ter sido colado pelo proprietário sem que tal fosse discutido com o artista.

AIP: Foi aplicada alguma camada de preparação dobre o papel antes de se fazer a pintura?

JS: Não foi aplicada nenhuma camada de preparação antes de se fazer a pintura

AIP: O branco da *Cenógrafa*já não é produzido e numa das visitas ao atelier disse-me que ainda usa um pigmento que compra na Casa Varela. É possível dar-nos a referência ou marca deste pigmento? Temos de usar o mesmo nas próximas reproduções para fazer as experiências.

JS: Este pigmento é comprado a peso, não tem uma referência. Usamos dois tipos: um de dióxido de titânio e outro de branco de zinco.

AIP: Podiam dizer-nos quando é que começaram a usar este novo pigmento?

JS: A partir de 2008.

AIP: Acerca de aplicação de uma fina camada de gesso acrílico sobre a camada de *Vulcano V7*/pigmento branco…Podiam dizer-nos quando é que começaram a usar esta nova técnica?

JS: A partir de 2004

AIP: Quanto tempo é que esperam antes de aplicar esta camada mais fina?

JS: Isso varia. Normalmente, o menor tempo possível…assim que está seca.

Appendix II: Analytical techniques and methods

Colorimetry: the measurement of colour

The CIE system provides a standardized procedure for measuring and quantifying the perception of colour. In the CIELAB system L*correlates with the lightness (L*=100 corresponds to a perfect white; L*=0 corresponds to a perfect black.[142] The coordinate a* correlates with red (+a*) and green (-a*) while the coordinate correlates with yellow (+b*) and blue (-b*).[142]

Colour determinations were made using a Datacolour International colorimeter (Microflash). The optical system of the measuring head uses diffuse illumination from a pulsed Xenon-arc lamp, with 10º viewing angle geometry; the reference source was D65. Calibration of the equipment was performed with bright white and black standards.

The differences in the coordinates between unaged an aged samples were calculated as followed:

$\Delta L^* = L^*_{aged} - L^*_{unaged}$ - a positive value indicates a lighter sample after aging; a negative value indicates the sample is darker;

$\Delta a^* = a^*_{aged} - a^*_{unaged}$ - a positive value indicates a redder sample after aging; a negative value indicates the sample is greener;

$\Delta b^* = b^*_{aged} - b^*_{unaged}$ - a positive value indicates a yellower sample after aging; a negative value indicates the sample is bluer.

ΔE^* was also calculated using the expression:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

If $\Delta E=1$ then the difference is only perceptible when the two samples are put side by side; if $\Delta E=2$ then the difference is clearly visible; if $\Delta E>5$ the difference is definitively visible even without confrontation between samples.[144]

For each Lab* value the mean of three measurements and the associated standard deviation was calculated. Measurements were taken on the same area of the sample to be studied with the aid of a positioning mask. In artificial and natural aging studies the Δ values were obtained between values of the reference unaged sample and corresponding aged sample.

Diffuse reflectance spectra (DRS)

Diffuse reflectance spectroscopy locates the main regions of absorption of a material and provides information on the energy, width and intensity of absorption bands. The plots of diffuse reflectance (r) against photon energy can be converted to plots of the Kubelka-Munk function f(r) against wavelength (λ in nm) and photon energy ($h\nu$ in eV), f(r) being defined by

$$F(r) = \frac{k}{s}$$

where *k* is the absorption coefficient and *s* is the scattering coefficient. Because *s* varies slowly with wavelength, f(*r*) provides a good representation of the absorption spectrum of the material.[145]

DRS were acquired with a UV-2501 UV-vis spectrophotometer (Shimadzu) with an integration sphere. Baseline correction was done using a calibrated sample of barium sulphate. Absorption spectra from the pure emulsions were obtained with free films. Absorption spectra of unaged and naturally aged pigmented paints were acquired in films applied either in glass slides or, cotton canvas.

Mass loss

Sample weight was measured at a Sartorius CP225 D micro analytical scale. Measures were taken from the glass slide samples and mass loss was determined by comparison of the irradiated samples before and after exposure to irradiation. The samples were kept in a desiccator prior to weighing and three measurements were taken for each sample.

Extraction and solubility

Solution of a polymer occurs in two stages: diffusion of the solvent through the polymer matrix, forming a gel; dispersion of the polymer macromolecules into solution. Even some linear (as opposed to crosslinked, network polymers) show lack of solubility in a given solvent, which does not necessarily mean that the polymer has crosslinked. [11]

Several tests with different solvents (water, ethanol, acetone and chloform), extraction times (from 1h to 48h) and extraction methodologies (pre-extraction with other solvents e.g. water) were tested. For the terpolymer the soluble fraction of polymer in the film matrix was extracted with chloroform. Preliminary extraction tests showed an extraction period of 48hrs was needed to extract a significant quantity of the polymer from the films (≈72%±6). For the PVAc homopolymer a pre-extraction in water was adopted because preliminary extraction tests demonstrated an increased efficiency in the quantity of polymer extracted (≈70%±7) when compared to the amount of polymer extracted through simple immersion in chloroform for 48hrs (≈50%±2). Moreover FTIR analyzes of the remaining insoluble part showed that it consisted of polymer and additives.

The experiments showed best efficiency when 7mg of the pure emulsion and 10mg of paint films were soaked in Millipore water for circa 3hrs. Centrifugation at 3000rpm for 15min was used to separate the subsequent precipitate and supernatant. The precipitate was immersed in $CHCl_3$ for 48hrs and then filtered through pre-weighted membrane filters (0.45 μm). Vials and filters were kept in a desiccator and the difference in weight before and after filtration was used as a measure of the solubility and insolubility of the paint samples. Chain scission was monitored through the average molecular weight (M*w*) of the soluble fraction of the samples. Crosslinking was followed by measuring the quantity of the insoluble fraction (weight of the immersed sample minus the soluble faction).

Size exclusion chromatography: measuring the average molecular weight and its distribution

The physical properties of polymers are directly related to the size of the molecules present in the samples studied. Softening temperature, melting temperature, melt viscosity, tensile strength and toughness vary considerably with the molecular weight. Photodegradation can lead to chain scission and/or to crosslinking corresponding to differences in the molecular weight from unaged to aged samples.

In polymers an average molecular weight is determined because in the polymerization process it is impossible for all growing chains to terminate at the same time and with the same length.[11] Size-exclusion chromatography (SEC) is well known for the determination of molar mass distributions as it mainly responds to differences in molecular size, which is dominated by chain length/molar mass.[146]The method involves fractioning of the polymer based on the hydrodynamic volume of the molecules and comparison of the fractions obtained with samples of known absolute molecular weight through a calibration procedure.[11] Three parameters were determined with SEC [11]:

M_n, number average molecular weight

$$M_n = \frac{\Sigma \mathrm{N}_i \mathrm{M}_i}{\Sigma \mathrm{N}_i}$$

Where N_i is the number of molecules having a molecular weight M_i

M_w, weight average molecular weight:

$$M_w = \frac{\Sigma \mathrm{W}_i \mathrm{M}_i}{\Sigma \mathrm{w}_i} = \frac{\Sigma \mathrm{N}_i \ \mathrm{M}_i^2}{\Sigma \mathrm{N}_i \mathrm{M}_i}$$

Where W_i is the weight fraction of each species having a molecular weight M_i

M, polidispersity index:

$$M = \frac{\mathrm{M}_w}{\mathrm{M}_n}$$

The polydispersity index gives a measure of the narrow or of the wide average molecular weight distribution. If M=1 then the system is monodisperse, in a polydisperse system the narrower the molecular weight range, the closer are the values of M_w and M_n.

Molecular weight distributions were determined with a SEC Waters apparatus, which includes a solvent delivery system composed of a model 510 pump, a Rheodyne injector and a refractive index detector (model 2410). Separation was carried with a series of three Waters Ultrastyragel columns, of 10^3Å, 10^4Å and 10^5Å porosity. $CHCl_3$ was used as eluent with a flow rate of 1 ml/min and the operating temperature was kept at 30ºC. Universal calibration was performed with monodisperse PMMA standards (Polymer Laboratories) with Mw ranges from 1.14×10^3 to 6.59×10^6. Butyl-hydroxytoluene (BHT) was used as a reference substance. The values of Marke-

Houwinke-Sakurada constants used for the PVAc/$CHCl_3$ and PMMA/$CHCl_3$ pairs, were respectively K=0.0203ml/g; a=0.72 and K=0.00493ml/g; a=0.8 [113]. Waters software Millenium 32 was used for the calculation of average molecular weights (Mw and Mn) and polydispersity. Solutions (w/v) in $CHCl_3$ of 0.75% for the pure emulsions and of 0.85% for the paints were prepared and 200ml of sample solution was injected.

Micro-Fourier Transform Infrared Spectroscopy (*μ*-FTIR)

FTIR has been used extensively as an analytical tool to characterize synthetic paints [97] because specific functional groups give a spectral fingerprint of the analyzed material. Infrared (IR) spectra were acquired with a Nicolet Nexus spectrophotometer equipped with a Continuμm microscope (15x objective) and a MCT-A detector cooled by liquid nitrogen. Analyses were performed in the transmission mode in the films applied on the Si disks and in micro-samples previously compressed with a Thermo diamond anvil cell. A resolution of $8cm^{-1}$ and 128 scans in the wavenumber range of 4000-650cm^{-1} was used for spectra acquisition of micro-samples. A Thermo diamond anvil compression cell was used to compress the samples prior to analysis. A resolution of 4 cm^{-1} and 64 scans in the wavenumber range 4000-300cm^{-1} was used for samples applied in Si disks films. Dry pigment samples were characterized using KBr pellets created in a hydraulic press. The wavenumber range used was 4000-300cm^{-1} with a resolution of $8cm^{-1}$ and 64 scans. Removal of the CO_2 absorption (≈2300-2400cm^{-1}) and baseline correction were performed in the spectra obtained from the micro-samples. Origin software (OriginLab Corporation) was used to calculate values of peak centre (μ), area (A), and full width at half maximum (σ) by fitting with a Gaussian function the absorption peaks from the C=O stretching. Unless it is mentioned all values presented are the average of at least three spectra obtained in each sample.

Attenuated Total Reflectance Spectroscopy (ATR)

ATR is probably the most widely used method for surface analysis in polymers as the IR radiation penetrates into the sample a few micrometers. This analytical technique is therefore very useful to analyze the sample's surface. Attenuated total reflection-FTIR spectra were collected using a Smart Omni ATR device containing a single-bounce silicon crystal. Background and sample spectra were acquired for each sample on three diferent areas with a resolution of $8cm^{-1}$ and 128 scans in the wavenumber range of 4000-650cm^{-1}.

Raman Microscopy (*μ*-Raman)

Analyzes were performed with a Labram 300 Jobin Yvon spectrometer, equipped with a HeNe laser 17mW operating at 632.8 nm and a 532nm solid state laser. A 50x or a 100x Olympus objective lens was used to focus the laser beam in the point of interest. The laser power at the surface of the samples was varied with the aid of a set of neutral density filters (optical densities 0.3, 0.6, 1). Spectra are shown here as acquired, without corrections or manipulations.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS)

Pyrolysis combined with gas chromatography and mass spectrometry (Py-GC/MS) has been used extensively as an analytical tool in which large molecules are degraded into smaller volatiles species with thermal energy.[147] It has been widely used for the characterization of synthetic paints.[97] Chromatographic information of the pyrolysis products is used to determine the composition of complex polymeric materials and even of low-level additives in polymers.[147] Mass spectrometry with soft ionization methods allows analysis of intact polymer ions with no or little fragmentation.[146] Some additives can be thermally removed from the polymer before they degrade by heating the sample to a sub-pyrolysis temperature: the low molecular additives are desorbed before the polymer chains undergoes decomposition.[147]The polymer undergoes degradation at a set pyrolysis temperature and the pyrogram only contains peaks from the polymer itself.[147] Developments in the method have made it into a routine method not only for identification and differentiation of synthetic polymers but as well as for quantitative determination of monomers in copolymers.[147] Because the latex samples were separated into its components analysis of the PVAc copolymers studied was straightforward and it was possible to define if the emulsion was plasticized externally or internally.[97] Py-GC/MS has also been used to follow the ageing of PVAc emulsions by calculating the ratios of external plasticizer to ethanoic acid as a compound representative of the polymer chains.[16] Mass spectra for alkyl substituted phthalate esters are very similar.[80] Most phthalate esters do not give an intense parent ion in the mass spectra.[110] Also, all phthalates have in common the major fragments.[110] For example, major ions with m/z 167 and 149 correspond to phthalate acid and phthalate anhydride.[110] The key used to identify the phthalates present on the analyzed samples was the minor fragments as well as the retention time.[110]

Pyrolysis–gas chromatography–mass spectrometry was carried out with a Frontier Laboratories Ltd. PY-2020D microfurnace pyrolyzer with an Agilent Technologies 5975C inert MSD/7890A gas chromatograph/mass spectrometer. No sample preparation was necessary and a maximum of 100g of sample was used. For evolved gas analysis samples were put in stainless steel Eco-cup and were purged with helium for three minutes before heating in the microfurnace. The temperature was raised from 100ºC to 225ºC using a rate of 20ºC per minute in order to liberate first the additives excluding the mass spectral contribution of the polymer. A second temperature ramping from 100°C to 550°C at 20°C per minute resulted in the pyrolysis and evaporation of the polymer fractions. The mass spectrometer was scanned from 10-600 amu. A flow of inert gas, nitrogen, flushes the pirolyzates into the column where the components are separated. Ions were generated by electron-impact (EI) ionisation (electron energy 70 eV). The pyrolysis products are identified with GC/MS providing a fingerprint of the original polymer and copolymer composition.[147] Each peak from the gas chromatogram can be identified by its mass spectrum. Frontier F-Search 2.0 program with mass spectral libraries for polymers and their additives was used for compound identification.

Atomic Force Microscopy

AFM allows high-resolution study of the surface of samples as it gives a three-dimensional topographical imaging of the surface with a resolution in the Ångstrom range. AFM images were obtained in the tapping mode in air on areas of 50x50µm, 10x10µm and 2x2µm. Imaging was performed using a TT-AFM from AFMWorkshop equipped with an tripod-type scanner with a scan range of approximately 70×70×17µm. Silicon cantilevers with a resonant frequency of approximately 300 kHz (AppNano) were used. For each sample three different areas were examined. All images were collected at 512 pixel resolution and were processed, analyzed and displayed using Gwyddion 2.29 software. Prior to analysis the surface of the samples was cleaned of possible dust contamination with an argon-air flow.

Differential Scanning Calorimetry (DSC)

DSC has become the method of choice for quantitative studies of thermal transitions in polymers.[11] It measures the changes in heat capacity of the samples as a function of temperature.[148] T_g is a fundamental characteristic of a polymer as it relates to polymer properties and depends on the chemical nature of the polymer and molecular weight. Photodegradation leads to chemical changes which in turn lead to different T_g values. T_g is a function of the rotational freedom in the macromolecules, therefore whatever restricts rotation increases the T_g value.[11] If crossliking occurs there is a higher the molecular weight, the fewer the chain ends, which leads to a lower free volume in the polymer and consequently an increase in the glass transition temperature. Polarity also increases T_g, for instance chloro groups are more polar leading to increase dipole-dipole interactions between the macromolecules.

Glass transition temperatures of the pure binders and paint composites were determined using a Mettler DSC-30 with a TC10A controller. All measurements were performed using a heating rate of 5ºC per minute in an inert nitrogen atmosphere. Open aluminum pans were used for the analysis of c. 15mg of sample. Empty sample pans were used as blanks.

Thermogravimetric analysis (TGA)

The variation of weight from a sample when subjected to an increase in temperature can be measured by TGA giving information on: the amount of inorganic and organic components in pigmented paints; loss of plasticizers and additives; the substituent groups in the macromolecules.

Analysis were carried out in an TGA Perkin-Elmer Pyris under inert flowing nitrogen at the heating rate of 5ºC/min. Alumina was used as a reference material and all the samples were 25-30mg in a platinum crucible. All the runs were carried out between 50-600ºC.

Appendix III: Molecular characterization of vinyl binders and colored paints

3.1. Values used for μFTIR spectra interpretation and for Py-GG/MS chromatograms and mass spectra identification

Table A3.1: Wavenumber (in cm^{-1}) and band assignment for a PVAc film applied from solution in acetone.

Band assignment	Wavenumber
vC=O overtone	3452
v_{as}C-H (CH_3)	2971
v_{as}C-H (CH_2)	2926
vC=O	1740
δ_{as}C-H (CH_3), δC-H (CH_2)°	1434
δ_sC-H (CH_3)	1374
vC-O of (CO)O	1243
vC-C	1124
	1047
vC-O of (O-CH)	1023
vC-C#	947
ρ_rC-H (CH_2)*	796

° The methyl group has two deformation modes the antisymmetric and the symmetric deformation. The methylene group has a single H-C-H bond angle therefore a single deformation mode occurs at c.1450cm^{-1}. That is very close to the antisymetric bending of the CH_3 that occurs at c.1460cm^{-1}. [149] Therefore this band is probably an overlap of the stretching of both groups.

The calculated frequency for the vC-C is 1100cm^{-1}. However because the group is part of a molecule it can no longer vibrate independently. A displacement is caused by the groups of other molecules and will interfere with the vibration of the group. This mechanical coupling will always occur between C-C bonds so there is no simple C-C group stretching frequency and several IR bands in the range 1200-800cm^{-1} are expected to appear.[98]

*The ρrC-H of the methylene group is 810 cm^{-1} if the group is isolated and is c. 751cm^{-1} if it is coupled to other methylene groups in the polymer chain.

Table A3.2: Wavenumber (in cm^{-1}) and band assignment for the studied homopolymer emulsion and copolymers.

Band assignment	PVAc (solution Aldrich)	*V7* PVAc emulsion	VeoVa (Shell W-10)	PVAc-VeoVa emulsion (DM23)	PVAc-VeoVa emulsion (DM21)	*Imofan* Av44-11 (PVAc-VeoVa emulsion)	*Bizonte* (PVAc-VeoVa emulsion)
vC=O overtone	3452	3450	—	3457	—	—	3452
v_{as}C-H (CH_3)	2971	2963	2960	2964	2963	2963	2965
v_{as}C-H (CH_2)	2926	2939	2940	2933	2935	2935	2940
v_sC-H (CH_3)	—	2877	2880	2875	2873	2874	2877
vC=O	1740	1740	1750	1740	1740	1736	1740
δ_{as}C-H (CH_3), δC-H (CH_2)	1434	1433	1470	1434	1435	1433	1433
δ_sC-H (CH_3)	1374	1373	1390	1373	1373	1372	1373
vC-O of (CO)O	—	1288	—	—	—	1240	1243
	1243	1243	1210	1241	1241	—	—
vC-C	1124	1123	—	1124	1125	1123	1124
δC-H ring bending	—	1073	1140	—	—	1073	1074
vC-C	1047	1047	1040	—	—	1046	1046
vC-O of (O-CH)	1023	1022	1020	1023	1022	1022	1022
vC-C	—	981	—	—	—	—	—
	947	950	950	946	946	946	947
	—	—	870	—	—	—	—
ρ_rC-H (CH_2)	796	796	—	796	796	796	795

Table A3.3: Reference wavenumber values (in cm^{-1}) and band assignment for the acrylic binders identified in the case studies as presented in [2].

	p(nBA-MMA)	p(EA-MMA)
vC-H	2961	2985
	2938	2954
	2978	2910
	2847	2878
vC=O	1732	1733
δC-H	1466	1465
	1452	1449
	1387	1383
	1361	—
	1344	—
vC-O and vC-C	—	1297
	1240	1239
	1170	1178
	1150	1162
	1067	1118
	1027	1029
	992	—
	963	—
	947	—
C-H rock	844	854
	756	761

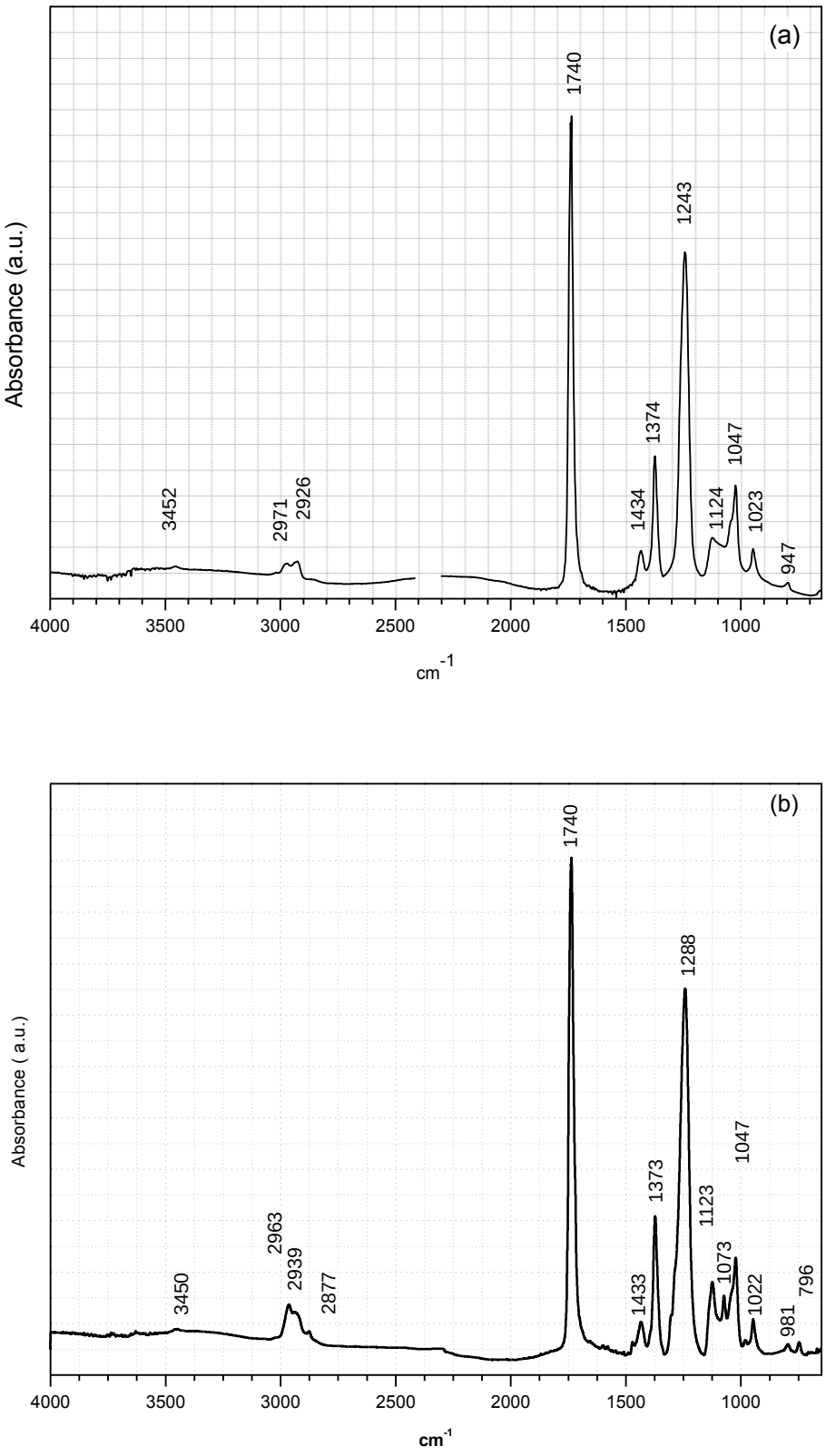

Fig. A3.1: Infrared spectrum of (a) a PVAc film cast from solution (*Aldrich*) and (b) a PVAc emulsion with DiBP (*Vulcano V7*).

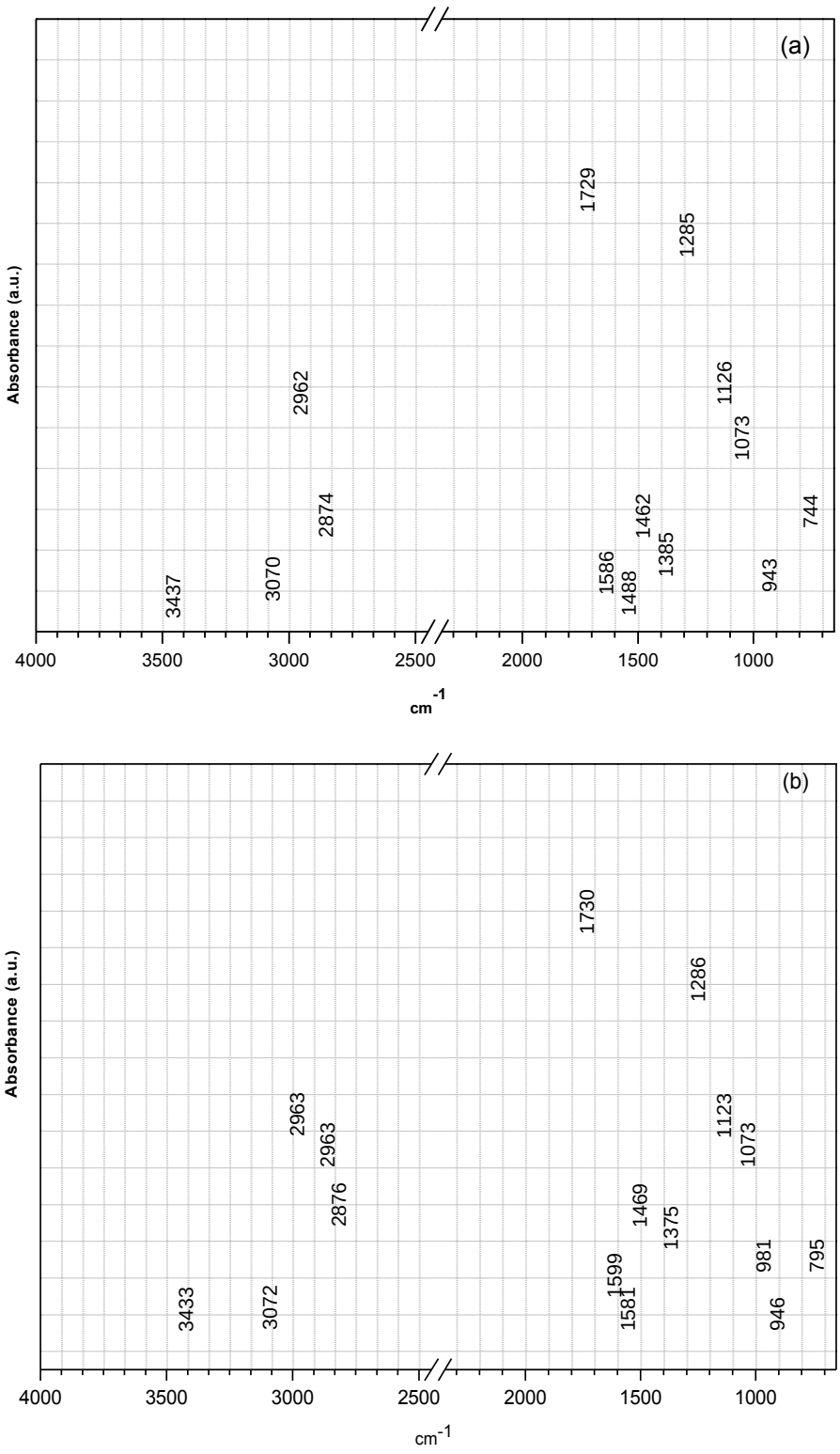

Fig. A3.2: Infrared spectrum of (a) dibutyl phthalate (b) diisobutyl phthalate.

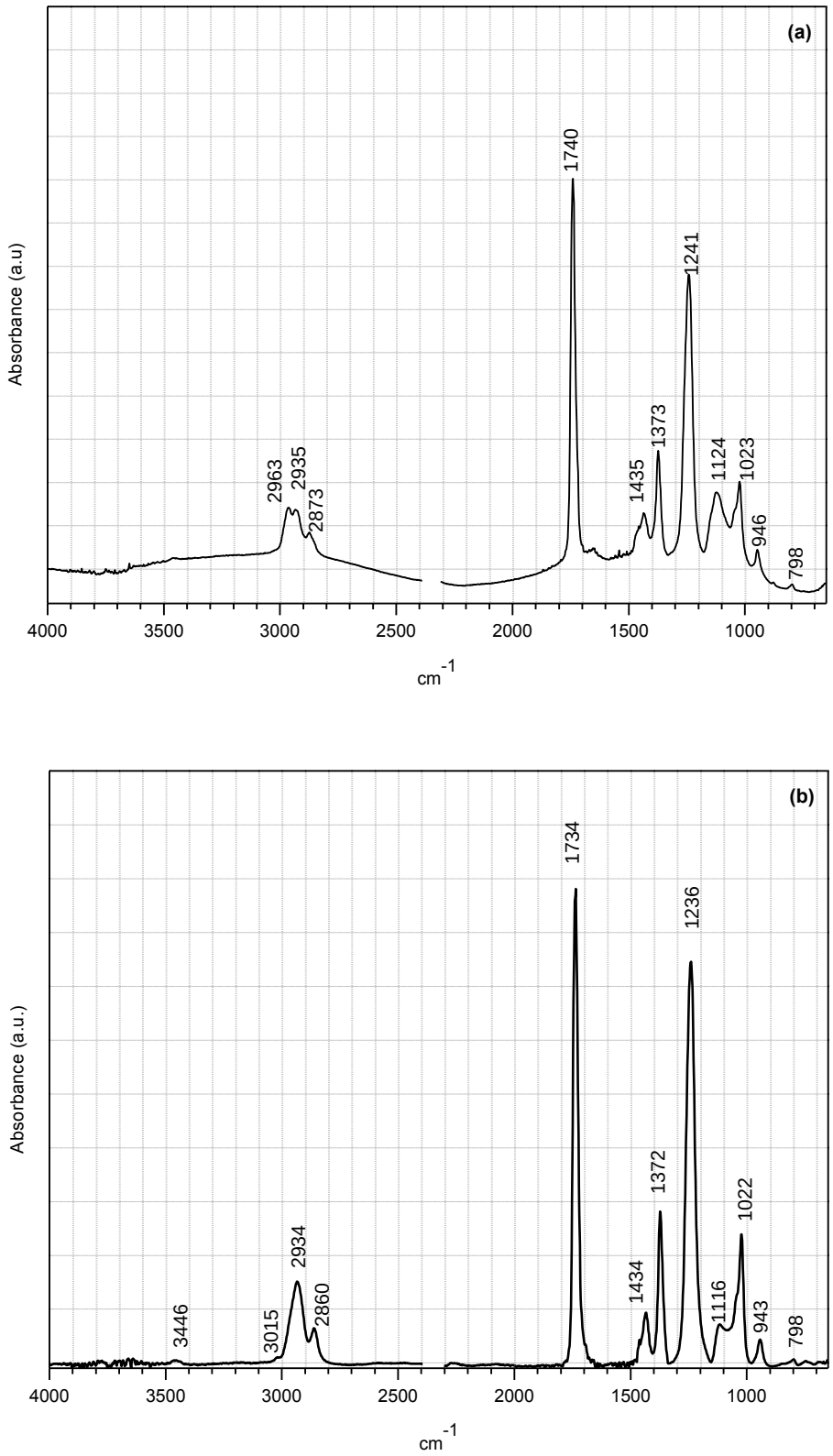

Fig. A3.3: Infrared spectrum of (a) a PVAc-VeoVa emulsion (*Resiquímica DM23*) and (b) the P(VAc-E-VC) terpolymer emulsion (*Vinamul 3469*).

Table A3.4: Molecular species produced on the pyrolysis of the ***Vulcano V7***, the corresponding retention time, molecular weight and m/z values.

Molecular species	Retention time	Mw	m/z
Carbon dioxide	1:50	44	44
Acetone	1:76	58	43,58
1,3 - cyclopentadiene	1:93	66	66,39
Acetic acid vinyl ester	2:13	86	86,43
Isobutyl alcohol	2:45	74	43,31,27,74
Acetic acid	2:72	60	60,43
Benzene	2:76	78	78,51
1-methyl-1,3 - cyclopentadiene	2:85	80	79,77,39
Acetic anhydride	3:38	102	43,15
Toluene	3:94	92	91,65
Ethylbenzene	5:03	106	91,106
styrene	5:37	104	104,78,51
2-propylbenzene	5:93	118	117,91
benzaldehyde	6:10	106	106,77,51
2-propenyl-benzene	6:72	118	117,91
1H-indene	6:90	116	116
2-methyl-1H-Indene	7:81	130	130,115
1,4 - dihydronaphthalene	7:95	130	130,115
naphthalene	8:13	128	128
1- methylnaphthalene	8:96	142	142,115
1,2-benzenedicarboxylic acid	9:04	166	104,76,50,148,117
Isobutyl benzoate	9:11	178	123,77,105
biphenyl	9:53	154	154,76
fluorene	10:90	166	166,82,39
stilbene	11:59	180	180,165,89,152
dihydro-antracene	11:94	180	179,165,89
9-methylene-9H-fluorene	12:07	178	178,76,89,152
Diisobutyl phthalate	12:32	149	149,223, 57, 104
Dibutyl phthalate	12:53	278	149

Table A3.5: Molecular species produced on the pyrolysis of the ***Sabu Tempera Acrílica*** binding medium, the corresponding retention time, molecular weight and m/z values.

Molecular species	Retention time	Mw	m/z
Carbon dioxide	1:54	44	44
Acetone	1:82	58	43,58
1,3 - cyclopentadiene	1:96	66	66,39
Methacryaldehyde	2:11	70	41,70,27
Benzene	2:79	78	78, 51
Acetic acid	2:85	60	60,43
1-butanol	2:91	74	56,41,31
E-3-penten-2-one	3:05	84	69,84,41
Acetic anhydride	3:40	102	43,15
Toluene	3:96	92	91,65,39
Butyl ester acetic acid	4:47	116	43,56,73
Ethylbenzene	5:05	106	91,106
styrene	5:38	104	104,78,40,51
cyclopropylbenzene	5:94	118	117,91
benzaldehyde	6:11	106	106,77,51
2-propenyl benzene	6:72	118	117,91
Indene	6:91	116	115,89,63
Acetophenone	7:07	105	105,77,120,51
1,2 - dihydronaphthalene	7:81	130	130,115,64
1,4 - dihydronaphthalene	7:95	130	130,115
naphthalene	8:13	128	128
2- methylnaphthalene	8:97	142	142,115
1,2-benzenedicarboxylic acid	9:04	166	104,76,50,148
1-methyl naphthalene	9:09	142	142,115
Butyl benzoate	9:42	178	105,123,77,56
biphenyl	9:53	154	154,76,51
fluorene	10:90	154	154,76
9-methylene-9H-fluorene	12:07	178	178,152,89,76
phthalate	12:53	278	149,205,57,104
Dibutyl phthalate	12:80	278	149,205,57,104
butyl 2-ethylhexyl phthalate	14:15	334	149,223
mono ethylhexyl phthalate	15:31	278	149,167,57,71,279

Table A3.6: Molecular species produced on the pyrolysis of the emulsion ***Imofan AV44/11***, the corresponding retention time, molecular weight and m/z values

Molecular species	Retention time	Mw	m/z
Carbon dioxide	1:53	44	44
1,3 - cyclopentadiene	1:96	66	66,39
Benzene	**2:79**	**78**	**78, 51**
Acetic acid	**2:89**	**60**	**60,43**
Acetic anhydride	3:40	102	43,15
Toluene	3:96	92	91,65,39
butyl ester acetic acid	4:47	116	43,56,73
Ethylbenzene	5:05	106	91,106
styrene	5:38	104	104,78,40,51
benzaldehyde	6:11	106	106,77,51
indene	6:91	116	115,89,63
acetic acid phenyl ester	6:96	136	94,136,43,66
1,2 - dihydronaphthalene	7:81	130	130,115,64
1,4 - dihydronaphthalene	7:95	130	130,115
naphthalene	8:13	128	128
neodecanoic acid	8:35	172	88,116,43,71,130
neodecanoic acid	8:39	172	88,116,43,71,130
2-ethyl-2,3,3 - trimethyl butanoic acid	8:47	158	102,57, 71,57, 41
neodecanoic acid	8:60	172	88,116,43,71,130
neodecanoic acid	8:64	172	88,116,43,71,130
2-ethyl-2,3,3 - trimethyl butanoic acid	8:67	158	102,57, 71,57, 41
biphenyl	9:53	154	154,76,51
diisobutyl phthalate	12:32	149	149,223, 57, 104
1-butyl 2-isobutyl phthalate	12:53	278	149
dibutyl phthalate	12:77	278	149

Table A3.7: Molecular species produced on the pyrolysis of the emulsion ***Bizonte***, the corresponding retention time, molecular weight and m/z values

Molecular species	Retention time	Mw	m/z
Carbon dioxide	1:52	44	44
Acetaldehyde	1:60	44	44,29,15
Acetone	1:77	58	43,58,15
1,3 - cyclopentadiene	1:94	66	66,39
Benzene	2:77	78	78, 51
Acetic acid	2:88	60	60,43
Acetic anhydride	3:39	102	43,15
2-methyl-4-pentenal	3:73	98	41,69,56,83
toluene	3:94	92	91,65,39
ethylbenzene	5:04	106	91,106
Styrene	5:37	104	104,78,40,51
ciclopropylbenzene	5:94	118	117,91
propylbenzene	6:02	120	91,12
benzaldehyde	6:11	106	106,77,51
2-propenyl benzene	6:72	118	117,91
indene	7:07	116	115,89,63
acetic acid phenyl ester	6:96	136	94,136,43,66
vinyl benzoate	7:65	148	107,77,51
2-methyl-1H-indene	7:81	130	130,115
Benzoic acid	7:90	122	105,122,77,51
1,2 - dihydronaphthalene	7:95	130	130,115,64
naphthalene	8:13	128	128
2-phenyl naphthalene	8:59	162	105,77
1-methyl naphthalene	8:97	142	142,115
butyl diethylene glycol acetate	9:24	204	87,57,43,101,72,29
biphenyl	9:53	154	154,76,51
diethylene glycol dibenzoate	9:96	314	105,149,77,51
Fluorene	11:41	154	154,76
diethylene glycol dibenzoate	11:70	314	149,105,77
9,10 - dihydrophenantrene	11:94	180	180,165,89,152,76
9-methylene-9H-fluorene	12:07	178	178,152,89,76
dibenzoate ethylene glycol	13:78	270	105,77,51
diethylene glycol dibenzoate	15:21	314	105,149,77
Dipropyleneglycol dibenzoate	15:24	342	105,163,77,207
diethylene glycol dibenzoate	16:28	314	105,149,77,51

Table A3.8: Molecular species produced on the pyrolysis of the emulsion ***Vinamul 3469***, the corresponding retention time, molecular weight and m/z values

Molecular species	Retention time	Mw	m/z
Hydrochloric acid	1:54	36	36
Carbon dioxide	1:53	44	44
Acetyl chloride	1:83	78	43,63,15
1,3 - cyclopentadiene	1:95	66	66,39
Benzene	2:79	78	78, 51
Acetic acid	2:82	60	60,43
1-methyl-1,3 - cyclopentadiene	2:88	80	79,77,51,31
cyclohexane	2:99	82	67,54,82,39
toluene	3:96	92	91,65,39
1, 3 - cycloheptadiene	4:12	94	79,94,39
3-methylene heptane ?	4:19	112	70,55,41,112
ethylbenzene	5:05	106	106,91
p-xylene	5:16	106	106,91,77,67,39
styrene	5:38	104	104,78,51
ciclopropylbenzene	5:94	118	117,91
propylbenzene	6:02	120	91,120,65
2-propenyl-benzene	6:72	118	117,91
Indane	6:82	118	117, 91
Indene	6:91	116	115,89,63
1,2 - dihydronaphthalene	7:81	130	130,115,64
1,4 - dihydronaphthalene	7:95	130	130,115
naphthalene	8:13	128	128
1-methyl-naphthalene	8:97	142	142,115
2-methyl-naphthalene	9:09	142	142,115
biphenyl	9:53	154	154,76,51
fluorene	10:90	154	154,76
9-methylene-9H fluorene	12:07	178	178,152,89,76

Table A3.9: Major molecular species produced o the pyrolysis of the artists paint ***Sabu Tempera Acrílica*** white, the corresponding retention time, molecular weight and m/z values.

Molecular species	Retention time	Mw	m/z values
Acetic acid	2:65	60	60,43,45
Benzene	2:78	78	78, 51
C_9H_{20}	4:97	128	43, 84,57,71,27
C_8H1_8	4:99	126	43, 70,55,83,29, 126
Ethylbenzene	5:05	106	106,91
$C_{10}H_{20}O_2$	8:38	172	88,116,43,71,130
$C_{10}H_{20}O_2$	8:43	172	88,116,43,71,130
$C_9H_{18}O_2$	8:53	158	102,57, 71,57, 41
$C_{10}H_{20}O_2$	8:67	172	88,116,43,71,130
$C_{10}H_{20}O_2$	8:71	172	88,116,43,71,130
$C_9H_{18}O_2$	8:74	158	102,57, 71,57, 41
Dibutyl phthalate	12:78	278	149,205,57,104

Table A3.10: Major molecular species produced on the pyrolysis of the artists paint **Sabu Tempera Acrílica** black, the corresponding retention time, molecular weight and m/z values.

Molecular species	Retention time	Mw	m/z values
Acetic acid	2:41	60	60,43,45
Benzene	2:78	78	78, 51
$C_{10}H_{20}O_2$	8:30	172	88,116,43,71,130
$C_{10}H_{20}O_2$	8:37	172	88,116,43,71,130
$C_9H_{18}O_2$	8:45	158	102,57, 71,57, 41
$C_{10}H_{20}O_2$	8:59	172	88,116,43,71,130
$C_{10}H_{20}O_2$	**8:63**	172	88,116,43,71,130
$C_9H_{18}O_2$	**8:65**	158	102,57, 71,57, 41
Dibutyl phthalate	12:77	278	149

3.2 The pigments and fillers

a) *Cenógrafa* white: Lithopone + $CaCO_3$

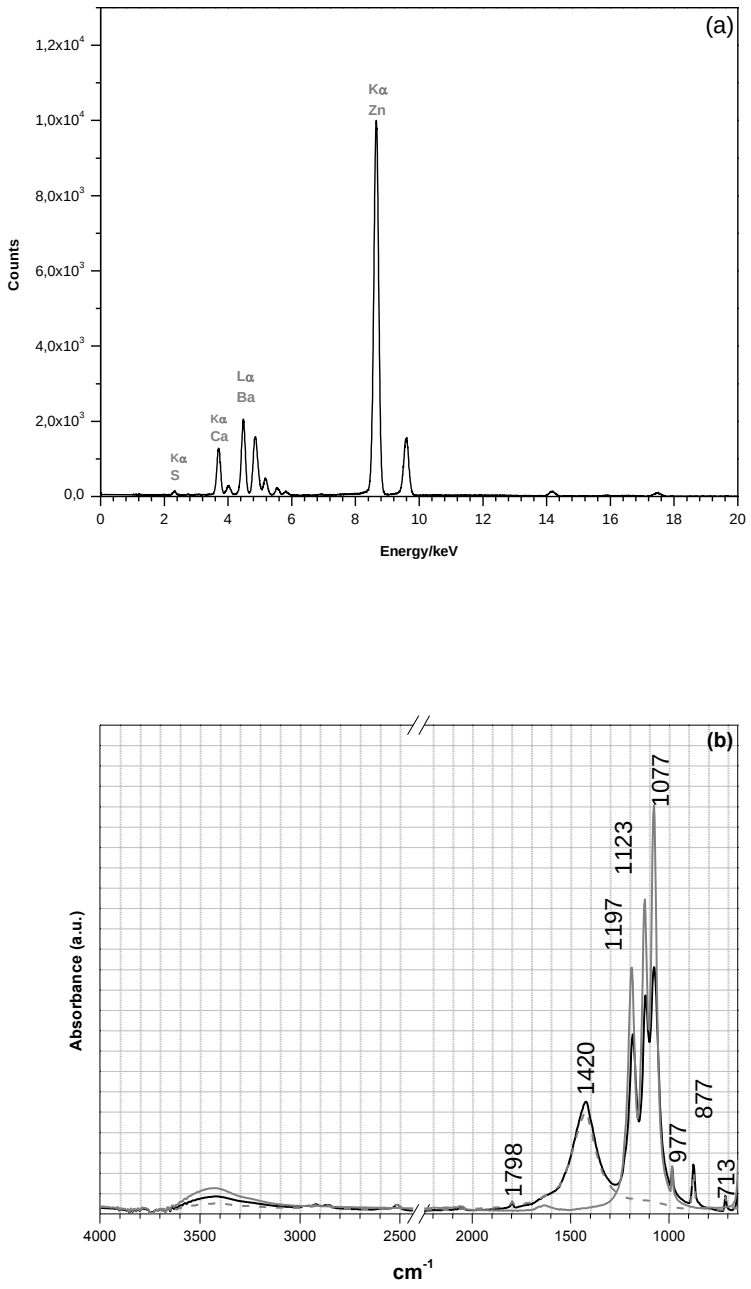

Fig. A3.4: (a) XRF spectrum of *Cenógrafa* white (b) Infrared spectrum of the mixture (—) and a reference spectra of $BaSO_4$ (—) and of $CaCO_3$ (…).

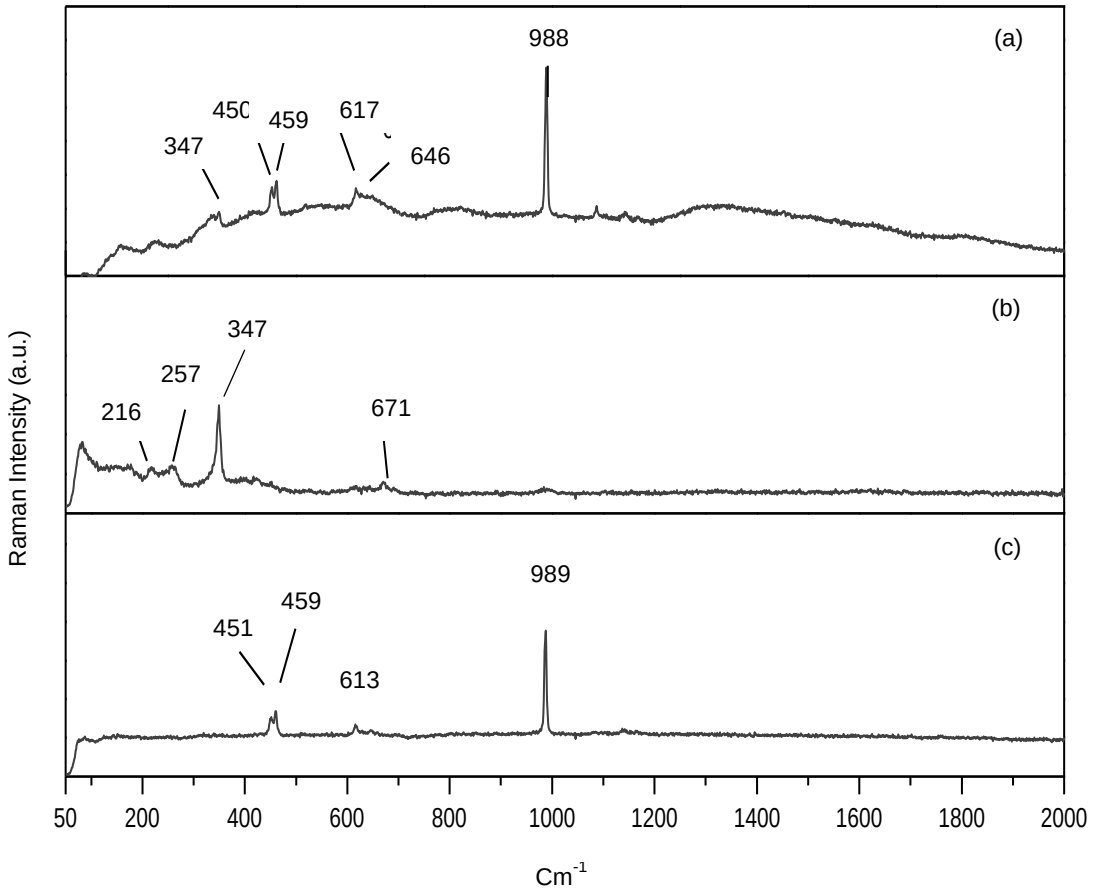

Fig. A3.5: Raman spectra of (a) *Cenógrafa* white (b) of zinc sulphide (c) and of barium sulphate.

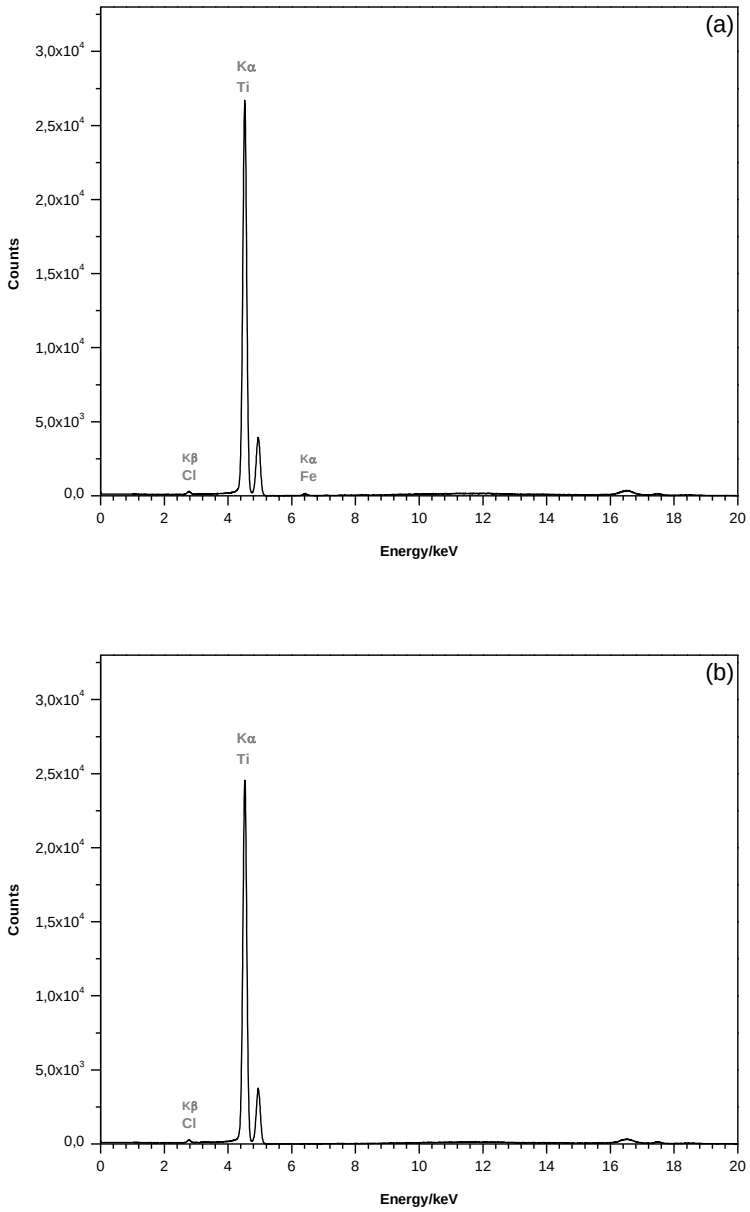

Fig. A3.6: XRF spectrum of (a) rutile and (b) anatase.

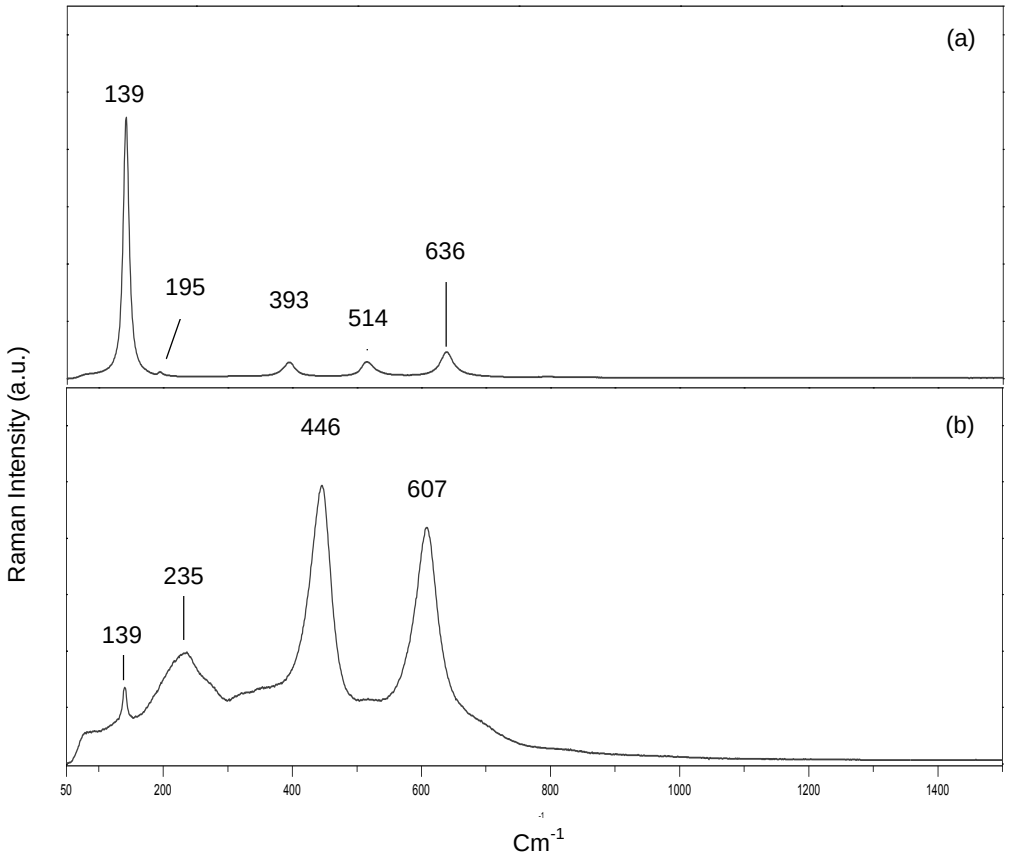

Fig. A3.7: Raman spectra of (a) TiO_2 anatase and (b) TiO_2 rutile.

c) Titanium white used since 2008

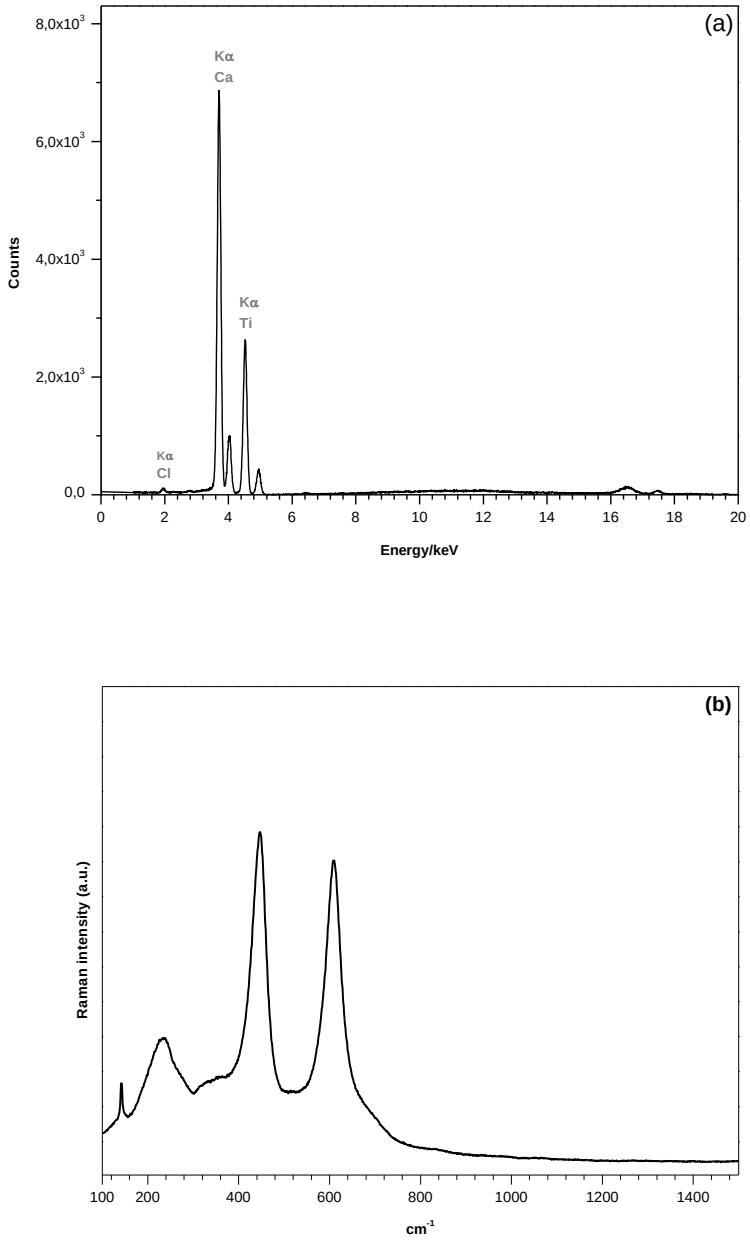

Fig. A3.8: XRF spectra (a) and Raman spectra (b) of TiO_2 rutile the white pigment used by Sarmento since 2008.

d) *Cenógrafa* Black: carbon black and iron black

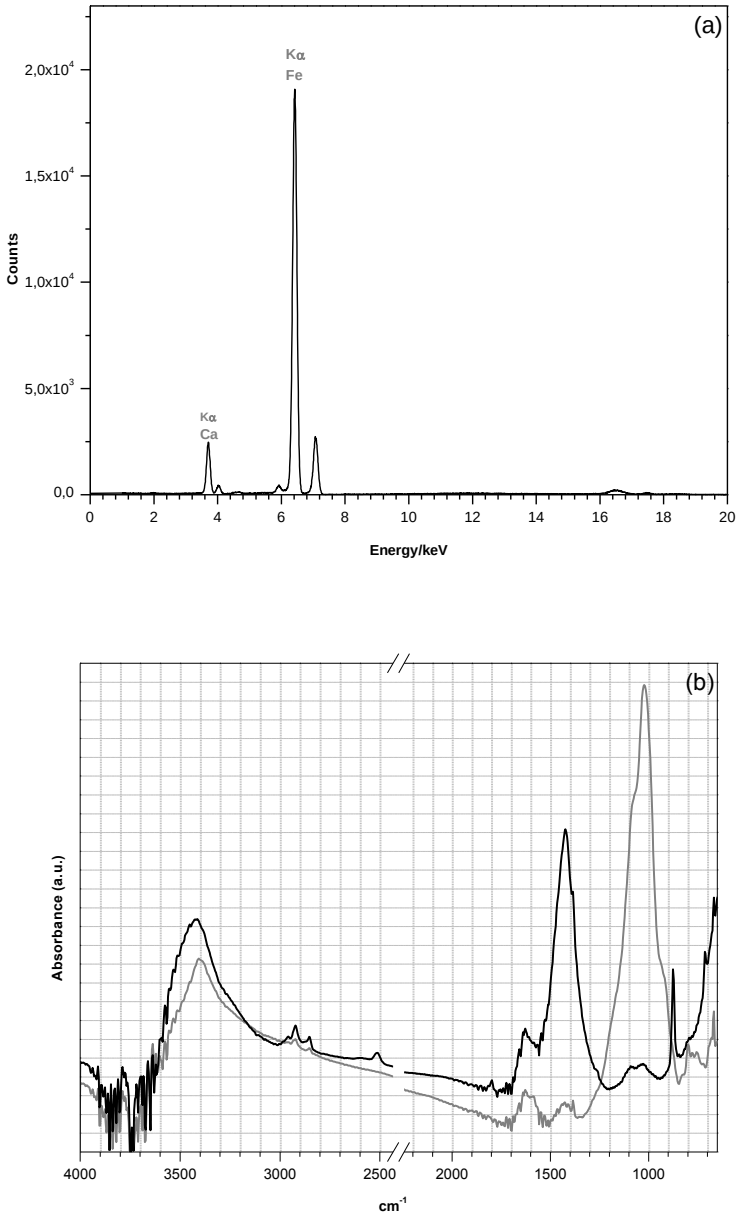

Fig. A3.9: (a) XRF spectra and (b) Infrared spectra of *Cenógrafa* black (—) and a carbon black pigment reference (—)

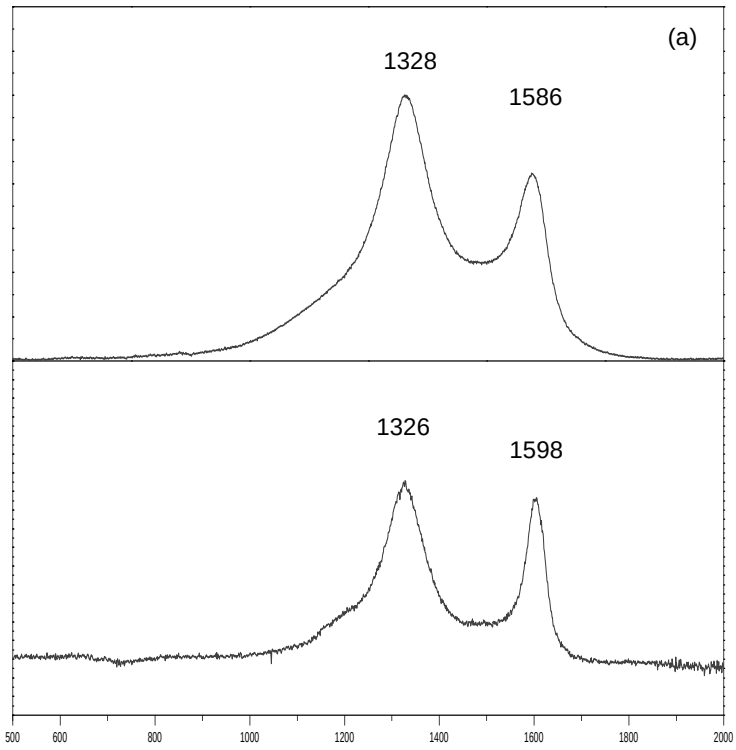

Fig. A3.10: (a) Raman spectra of *Cenógrafa* black and of (b) of a carbon black pigment reference

3.3: *Sabu* Tempera Acrílica.

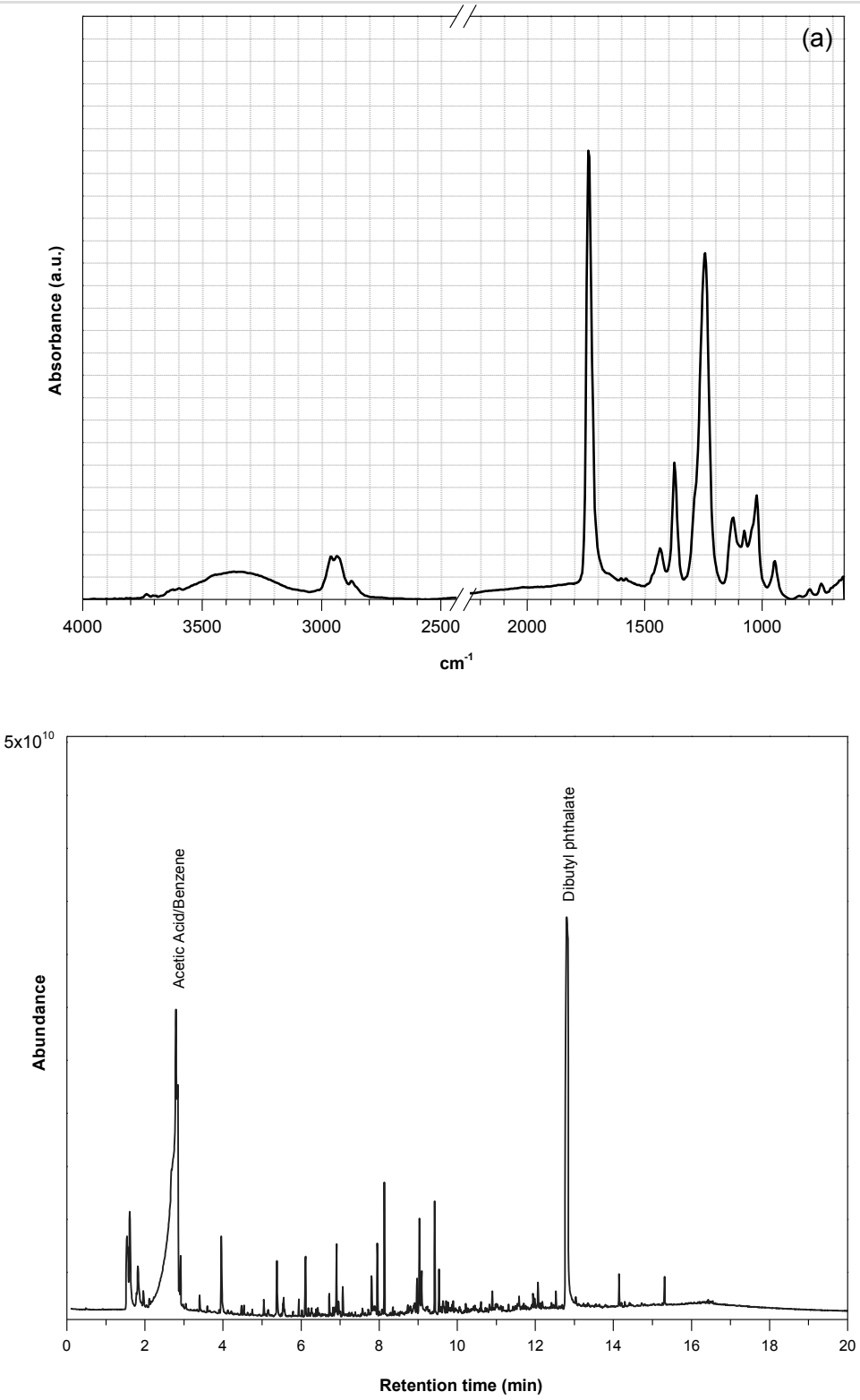

Fig.A3.11. (a) Infrared spectrum and (b) pyrogram of *Sabu Tempera Acrílica* a PVAc homopolymer.

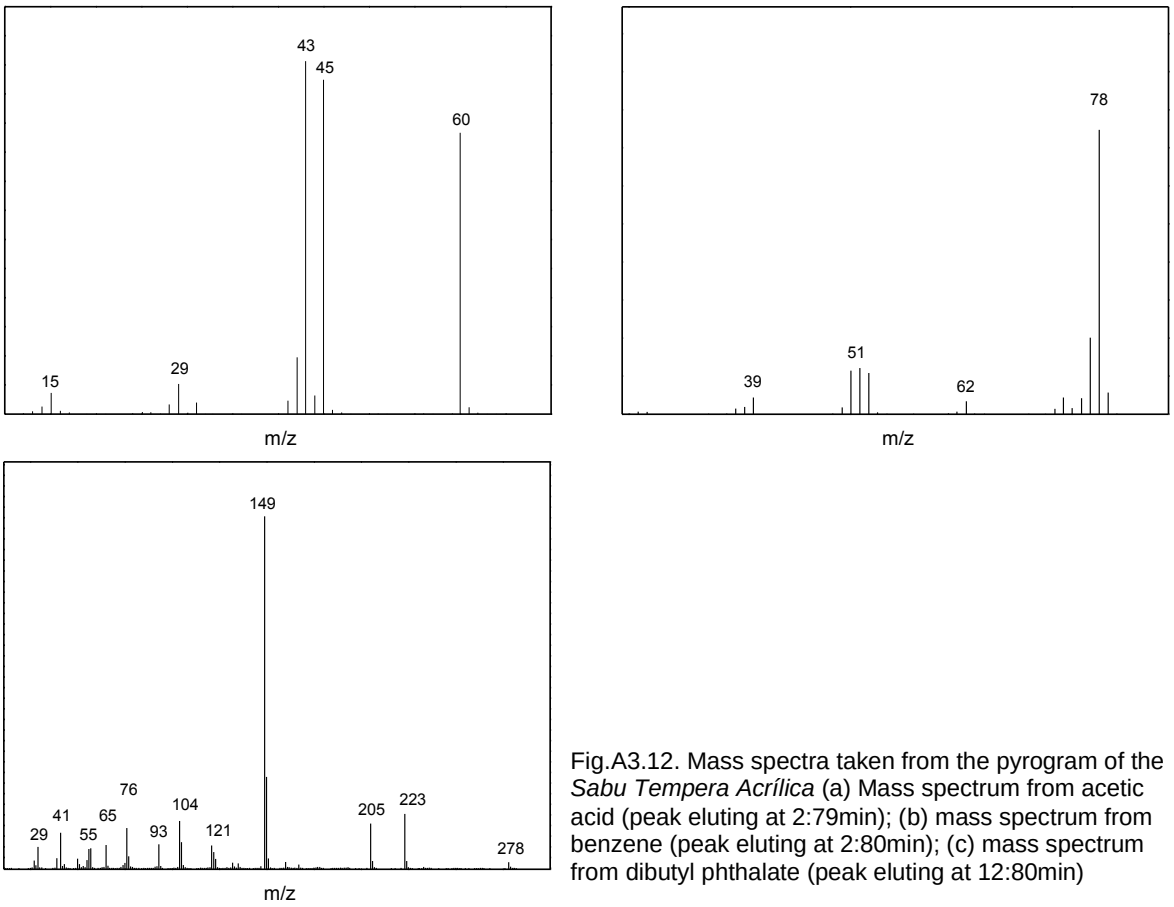

Fig.A3.12. Mass spectra taken from the pyrogram of the *Sabu Tempera Acrílica* (a) Mass spectrum from acetic acid (peak eluting at 2:79min); (b) mass spectrum from benzene (peak eluting at 2:80min); (c) mass spectrum from dibutyl phthalate (peak eluting at 12:80min)

3.4: *Imofan*: PVAc-VeoVa copolymer

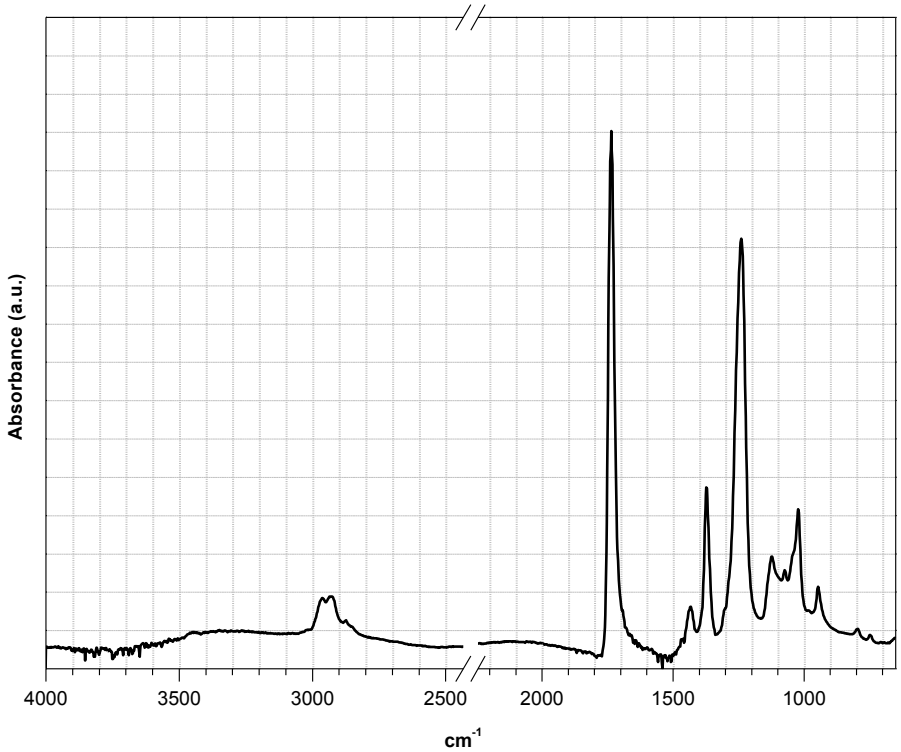

Fig.A3.13. Infrared spectrum of *Imofan AV44-11.*

3.5: *Bizonte* white glue

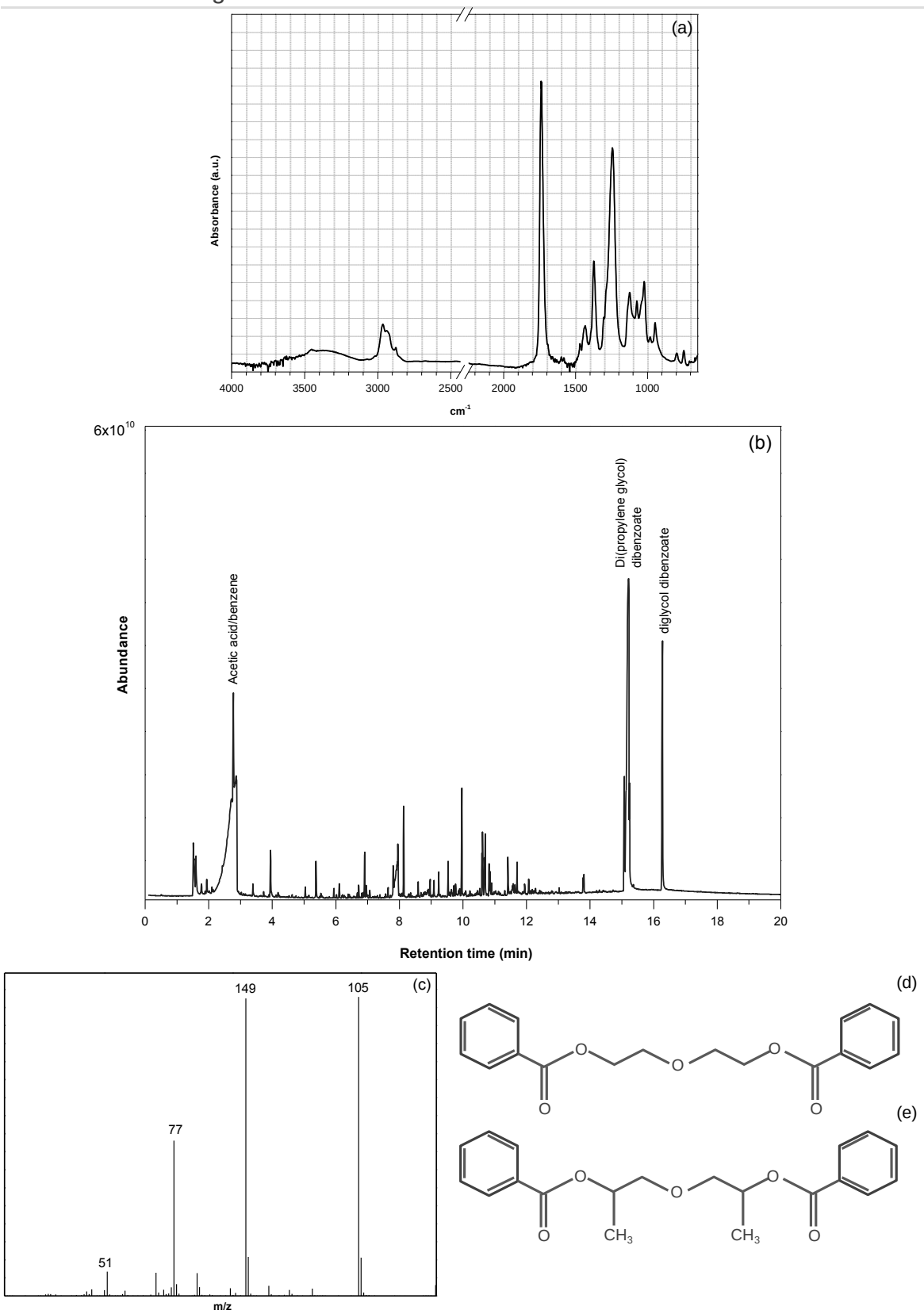

Fig. A3.14. (a) Infrared spectrum (b) pyrogram of *Bizonte* a PVAc homopolymer (c) Mass spectrum of diethylene glycol dibenzoate (peak eluting at 16:28min) (d) Dipropylene glycol dibenzoate. (e) Diethylene glycol dibenzoate (diglycol dibenzoate).

3.6. Old colored *Sabu*: PVAc-VeoVa copolymers

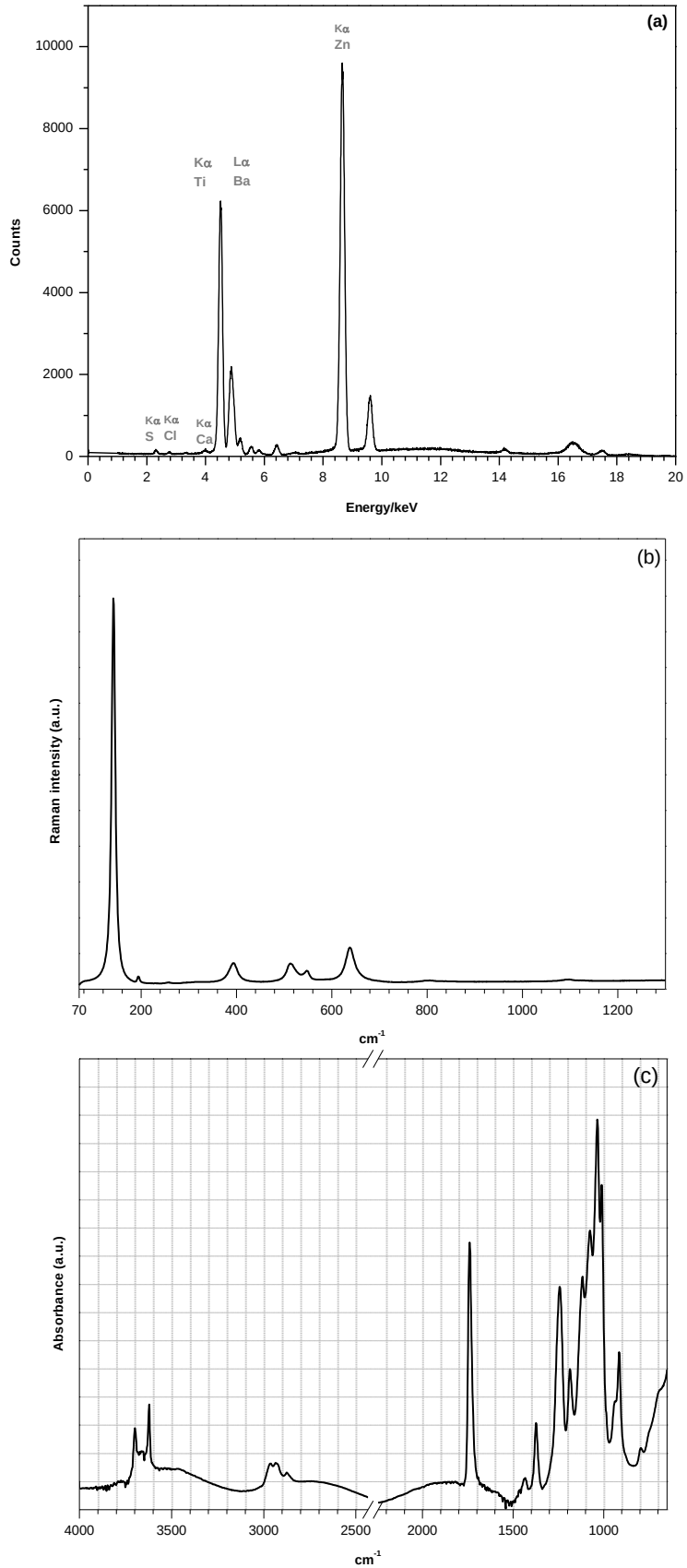

Fig. A3.15. Old *Sabu* white (a) XRF spectrum (b) Raman spectrum showing the presence of TiO_2 anatase and (c) Infrared spectrum, PVAc and kaolin.

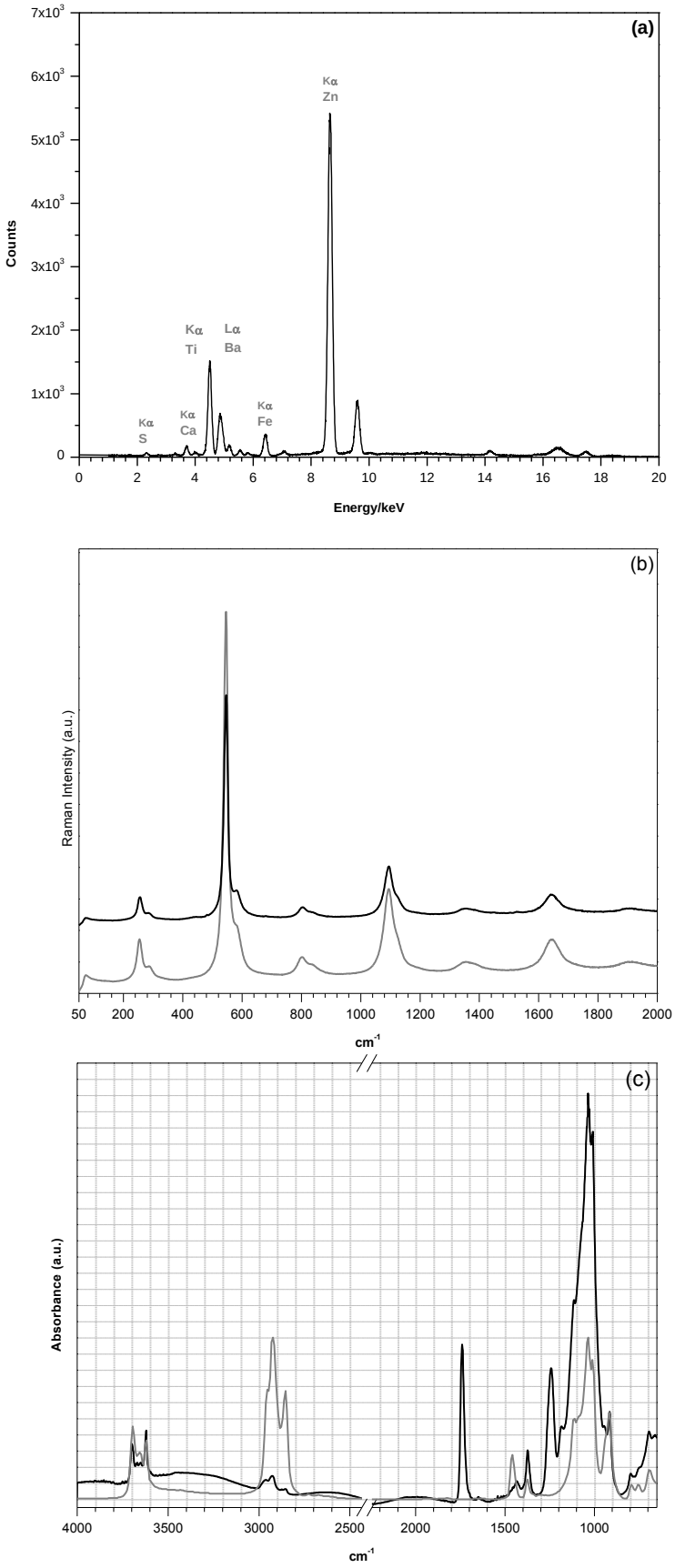

Fig. A3.16: *Sabu* blue (a) XRF spectrum (b) Raman spectrum of the blue pigment (—) and a reference spectrum of ultramarine (—) (c) Infrared spectrum of the PVAc binder and kaolin (—) reference spectra of kaolin (—)

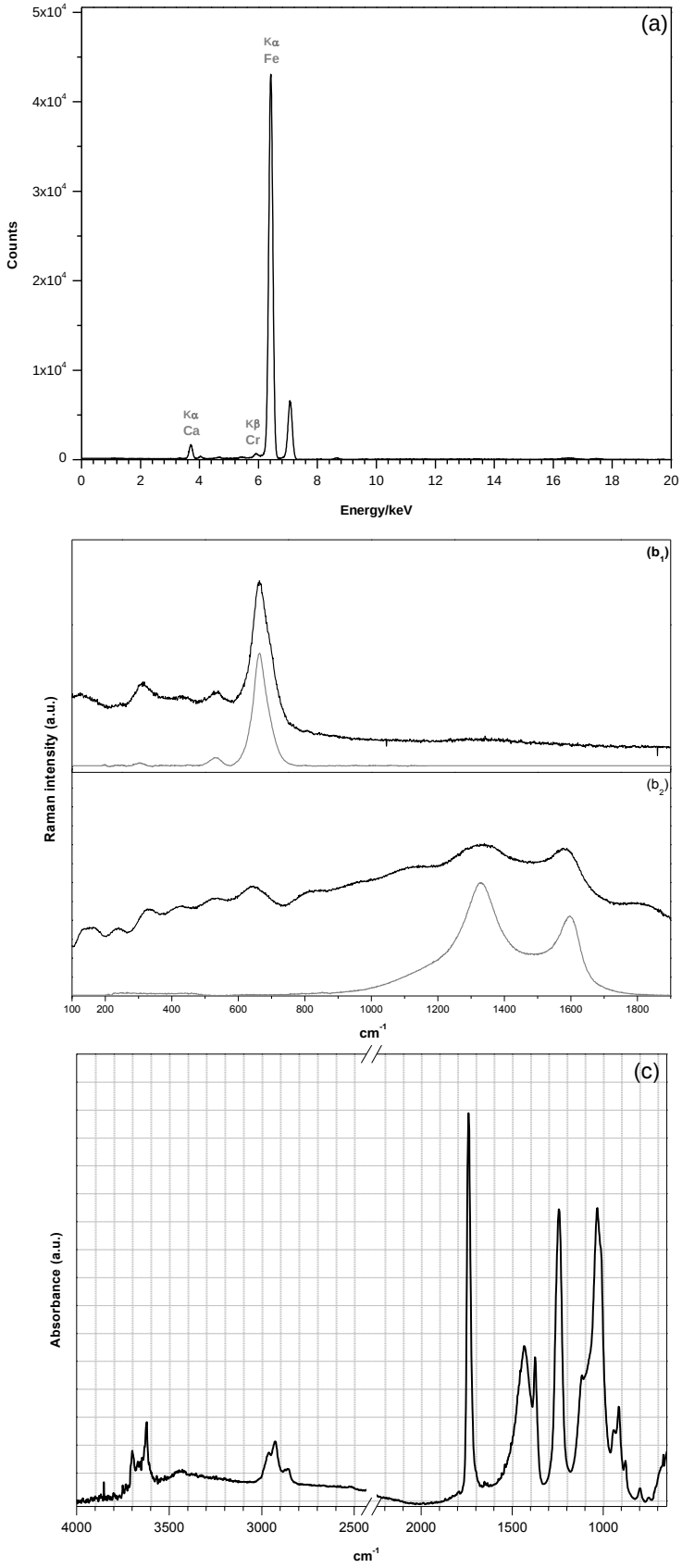

Fig. A3.17: *Sabu* black (a) XRF spectrum (b) Raman spectra of the two black pigments (b1) Iron oxide in the paint (—) and reference spectra of Fe_3O_4 (—) (b2) Carbon black in the paint (—) and reference spectra of C (—). (c) Infrared spectrum of PVAc, $CaCO_3$ and kaolin.

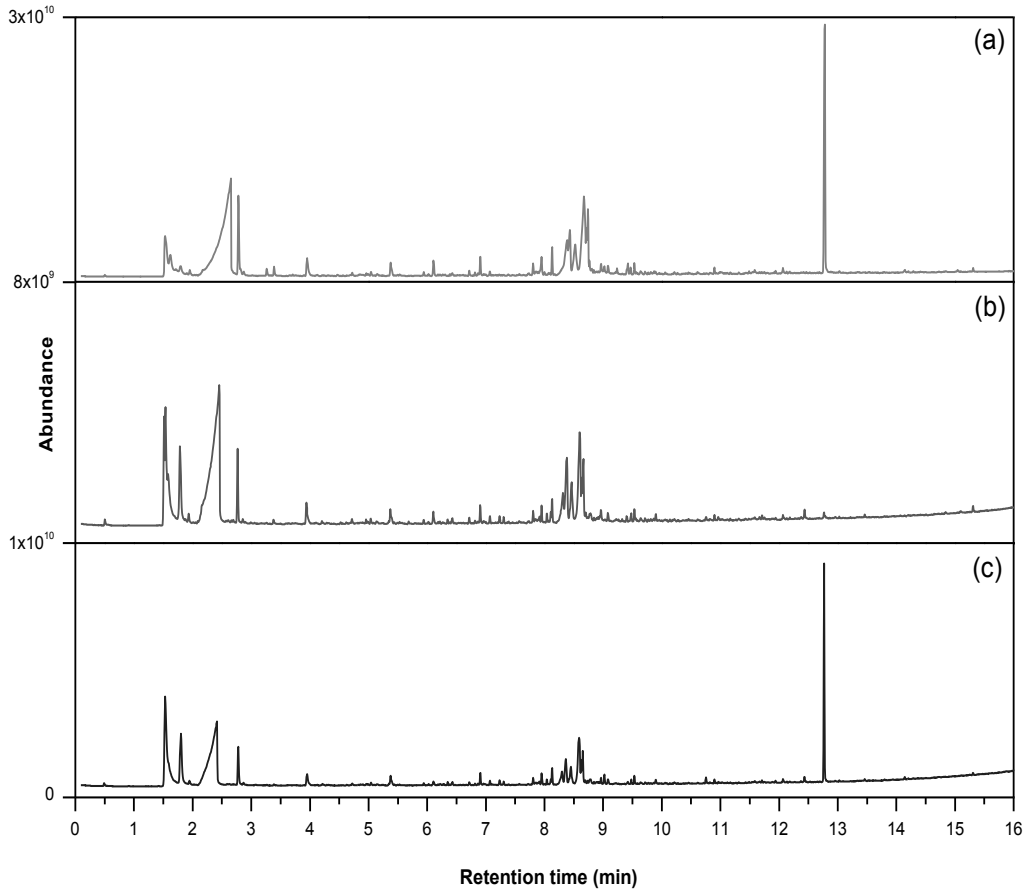

Fig. A3.18: a) to c) Pyrograms from *Sabu Tempera Acrilica* white (a), blue (b), black (c) all PVAc-VeoVa copolymers and dibutyl phthalate as an external plasticizer except for the blue paint where no external plasticizer was detected.

3.7. Modern colored *Sabu*: P(VAc-E-VC) terpolymers

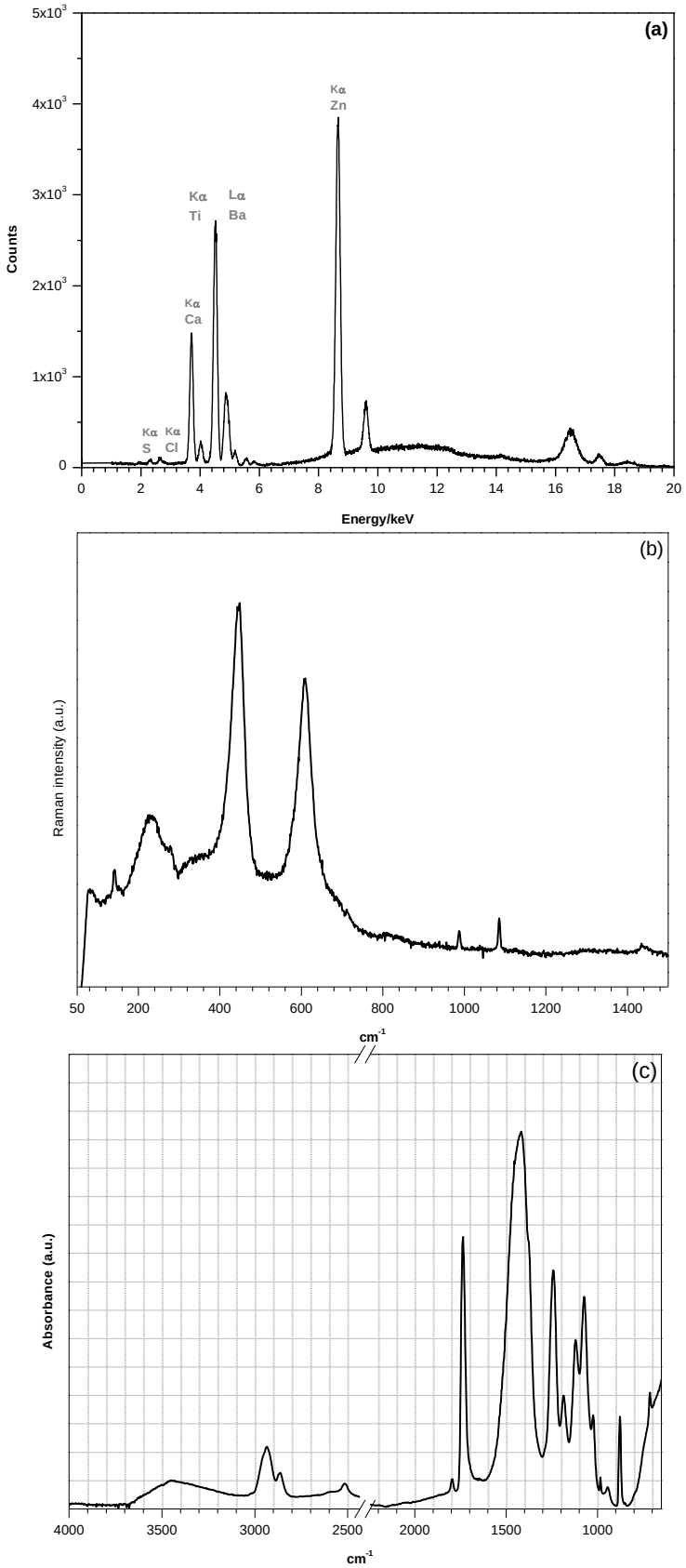

Fig. A3.19: Modern *Sabu* white (a) XRF spectra (b) Raman spectra of ruile TiO_2, $CaCO_3$ and $BaSO_4$. (c) Infrared spectrum of P(VAc-E-VC) binder, $CaCO_3$ and $BaSO_4$.

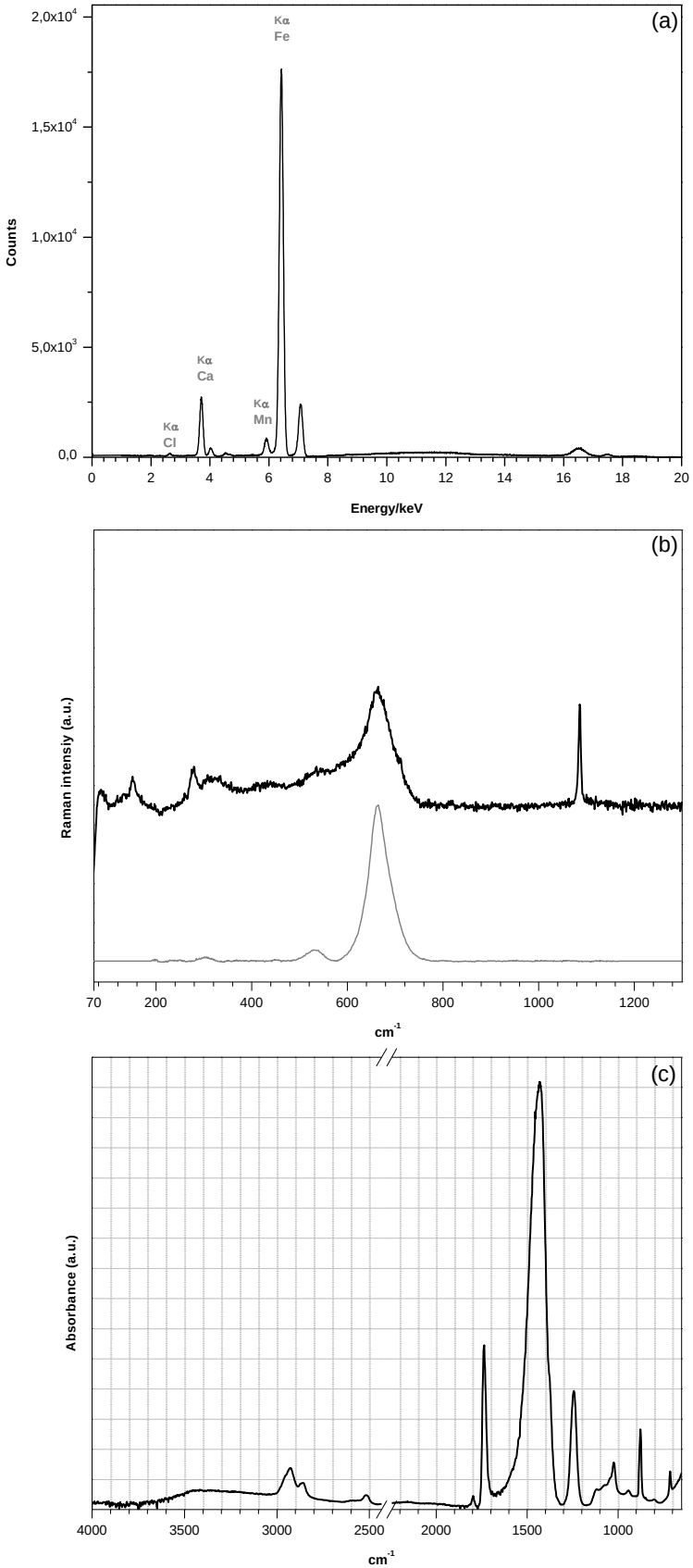

Fig. A3.20: Modern *Sabu* black (a) XRF spectrum (b) Raman spectra of Fe_3O_4 and $CaCO_3$ (—) and reference spectra of magnetite (—) (c) Infrared spectrum of P(VAc-E-VC) binder and $CaCO_3$.

3.8. *Rowney* PVAc paints

a) binding medium

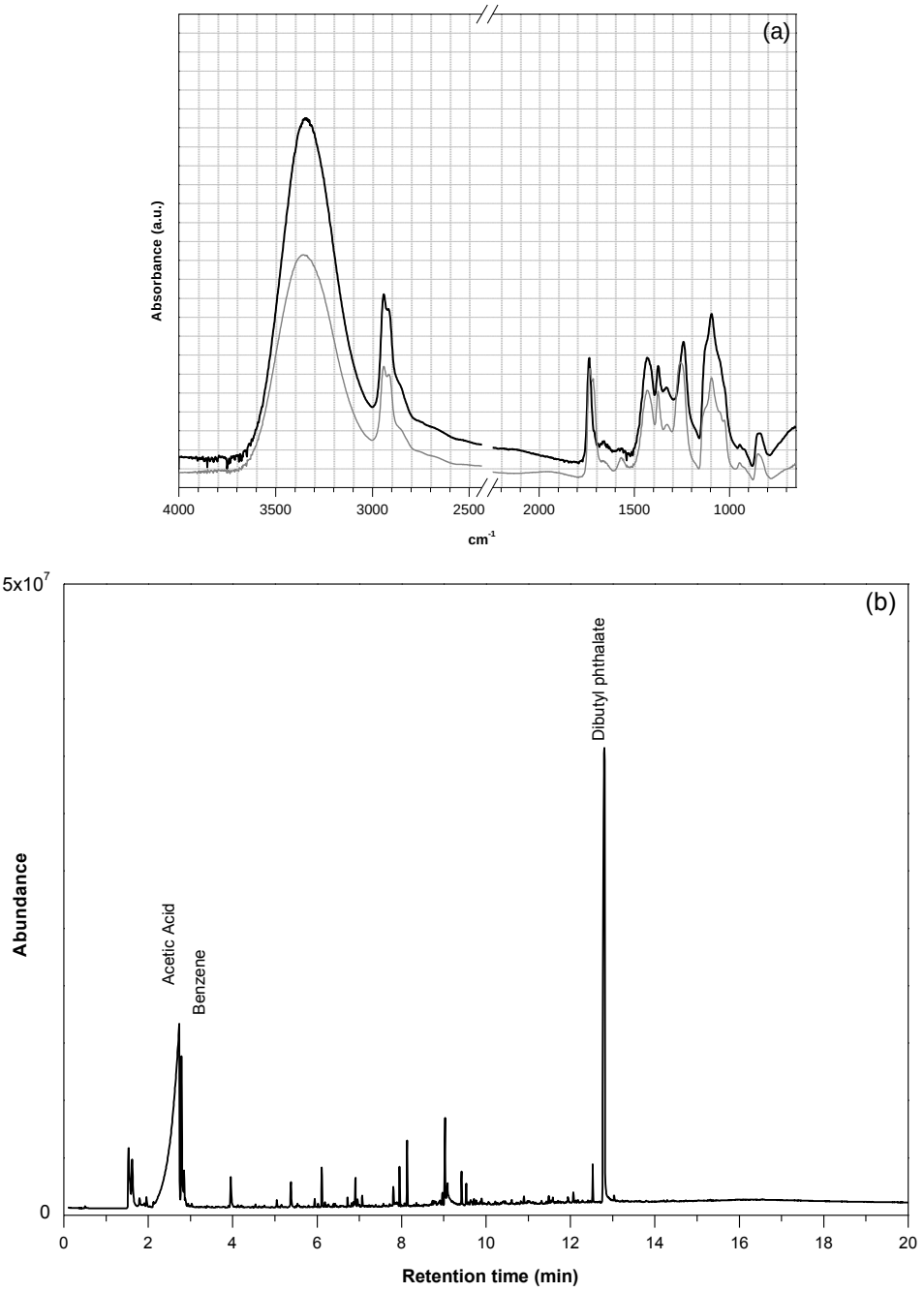

Fig. A3.21 (a) Infrared spectrum of *Rowney* hydrolyzed PVAc phase (—) and a reference spectrum of PVAl (—). (b) Pyrogram of the *Rowney* PVAc based binding medium.

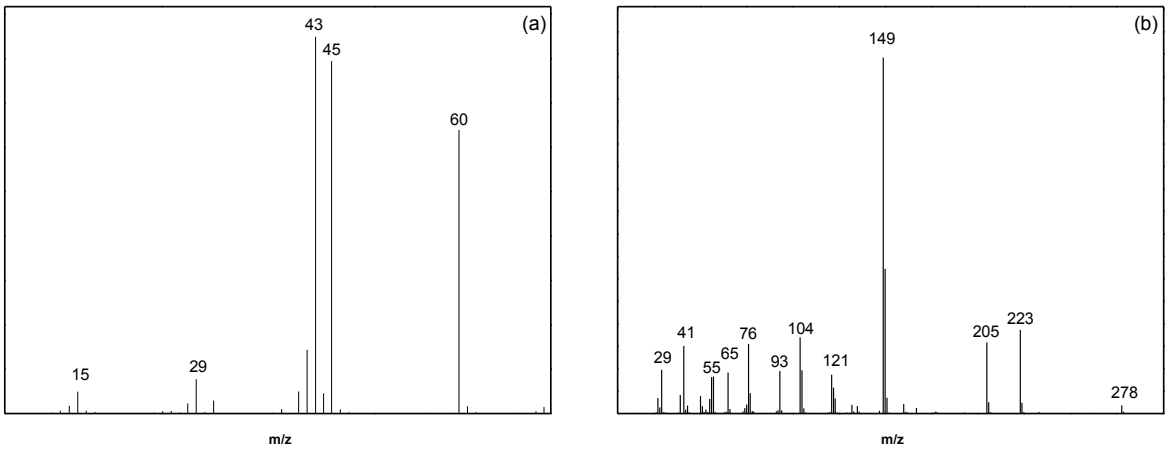

Fig. A3.22: (a) Mass spectrum from acetic acid (peak eluting at 2:73min); (b) mass spectrum of dibutyl phthalate (peak eluting at 12:80min) from the pyrogram in A3.21.

b) blue

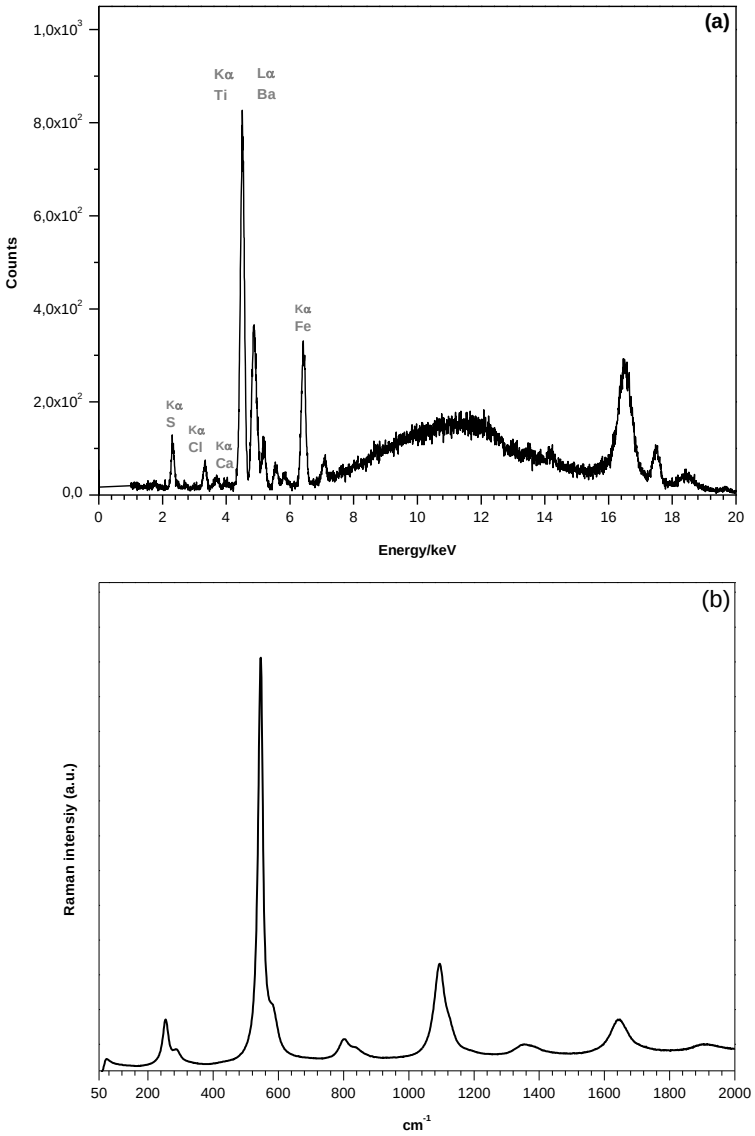

Fig. A3.23: (a) XRF spectrum (b) Raman spectrum of the anatase in the blue *Rowney* PVAc paint

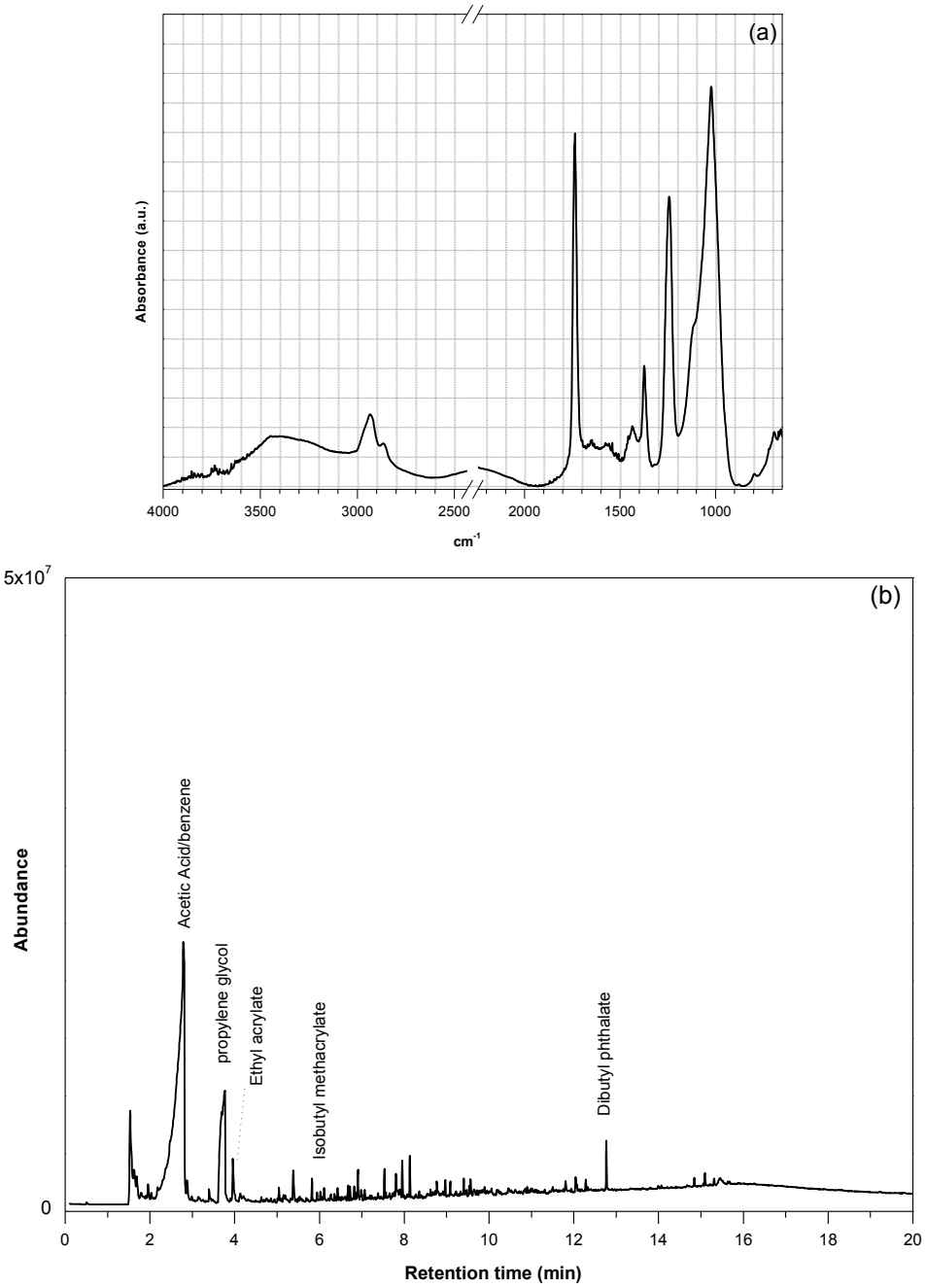

Fig. A3.24: (a) Infrared spectra revealing the PVAc and PE bands (b) Pyrogram of the *Rowney* blue paint

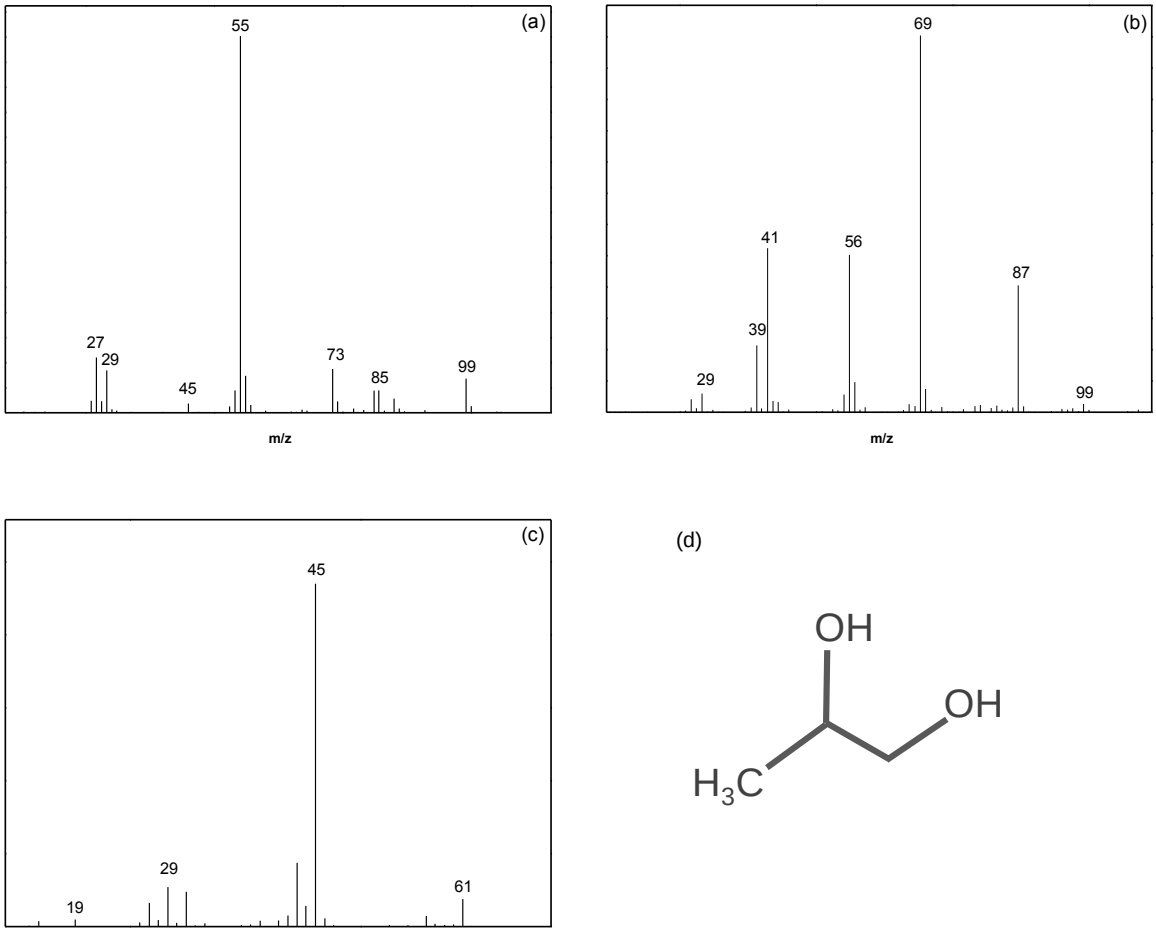

Fig. A3.25: (a) Mass spectrum from ethyl acrylate (peak eluting at 3:14min) (b) mass spectrum of butyl metacrylate (peak eluting at 5.82min) (c) mass spectrum of propylene glycol (peak eluting at c.3:77min) (d) propylene glycol.

c) Crimson

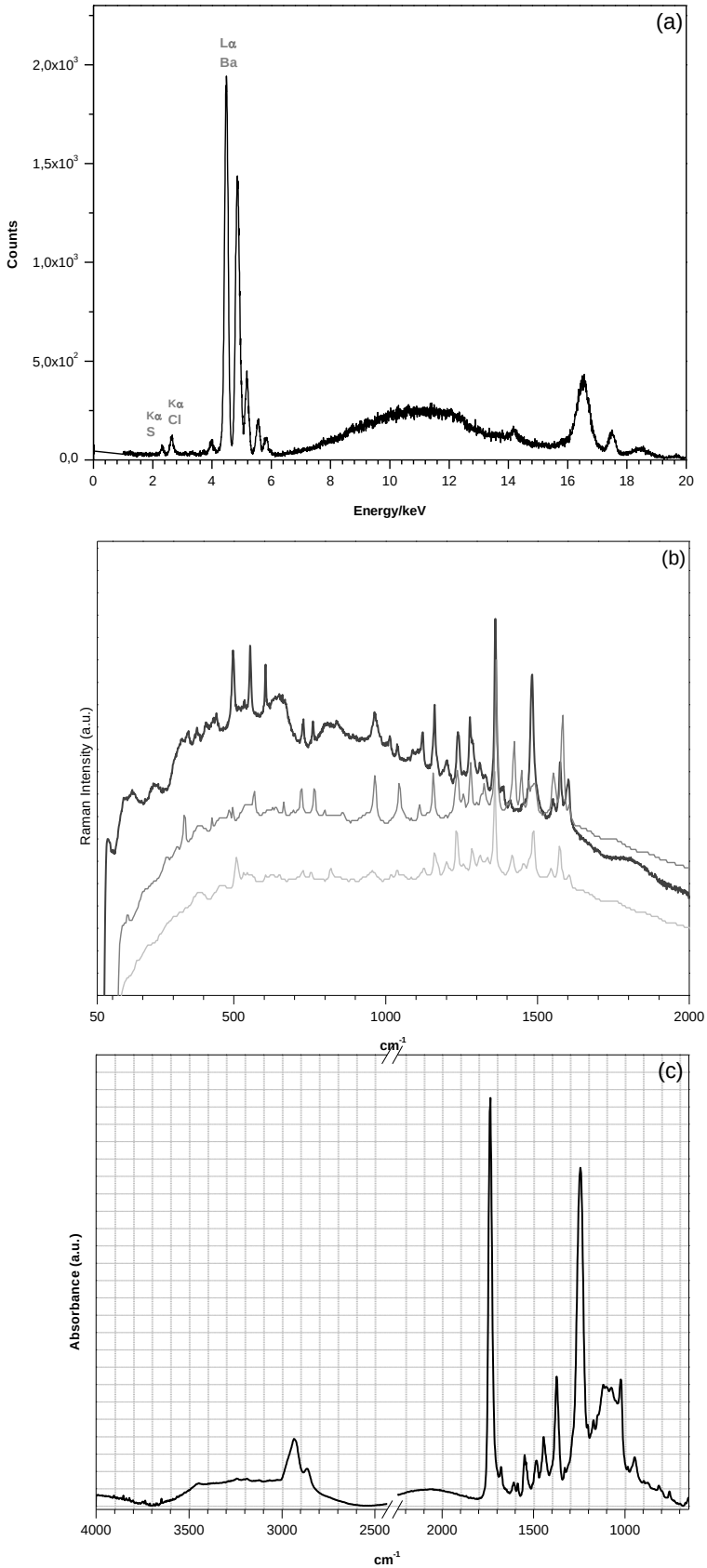

Fig. A3.26: (a) XRF spectrum (b) Raman spectra of *Rowney* crimson paint containing an azo red pigment (—) and reference spectra of PR10 (—) and PR11 (—); (c) Infrared spectrum revealing the PVAc and PE bands from the binder together with $BaSO_4$

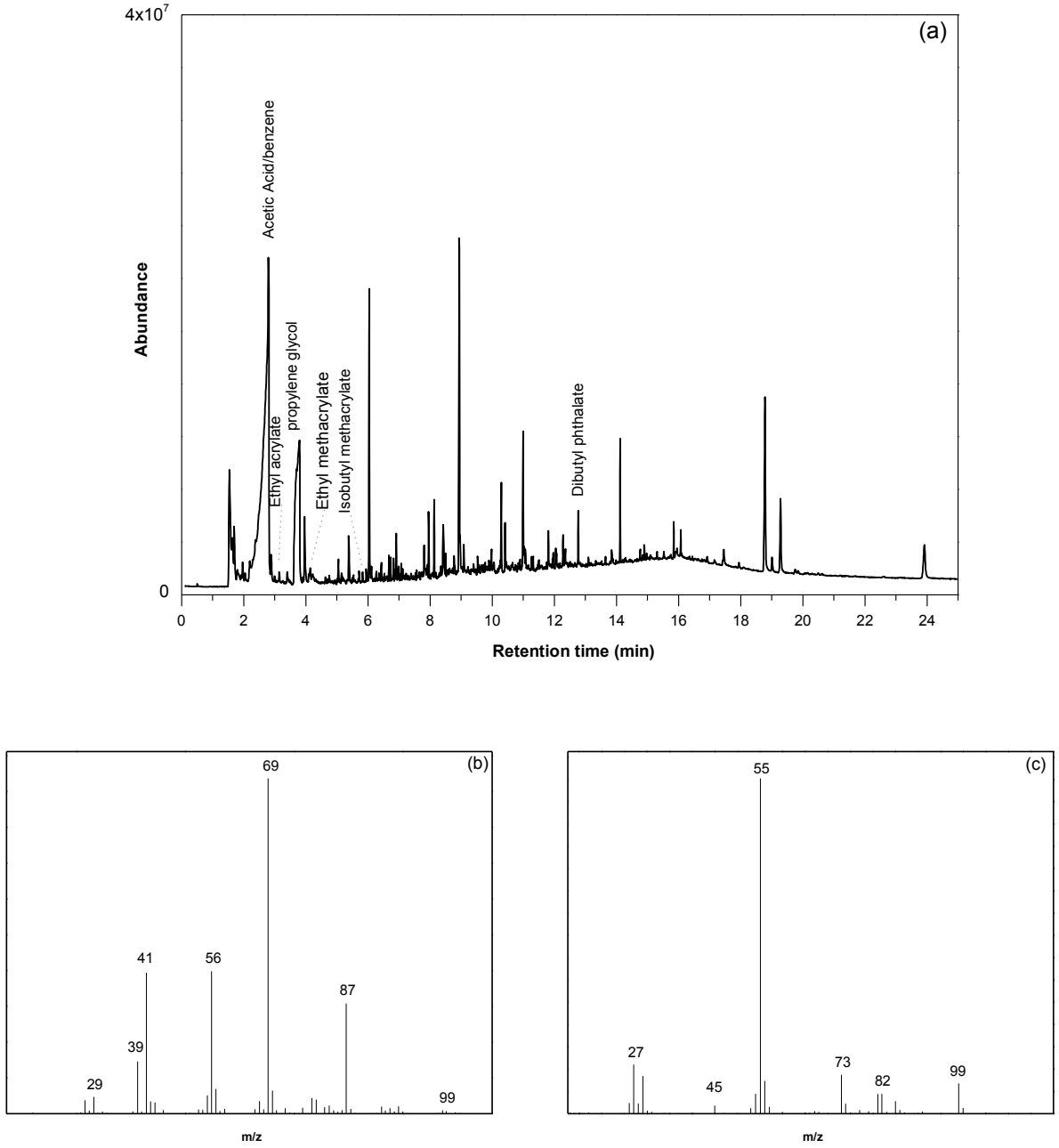

Fig. A3.27: (a) Pyrogram (b) mass spectrum of butyl methyl acrylate and (c) ethyl acrylate fractions.

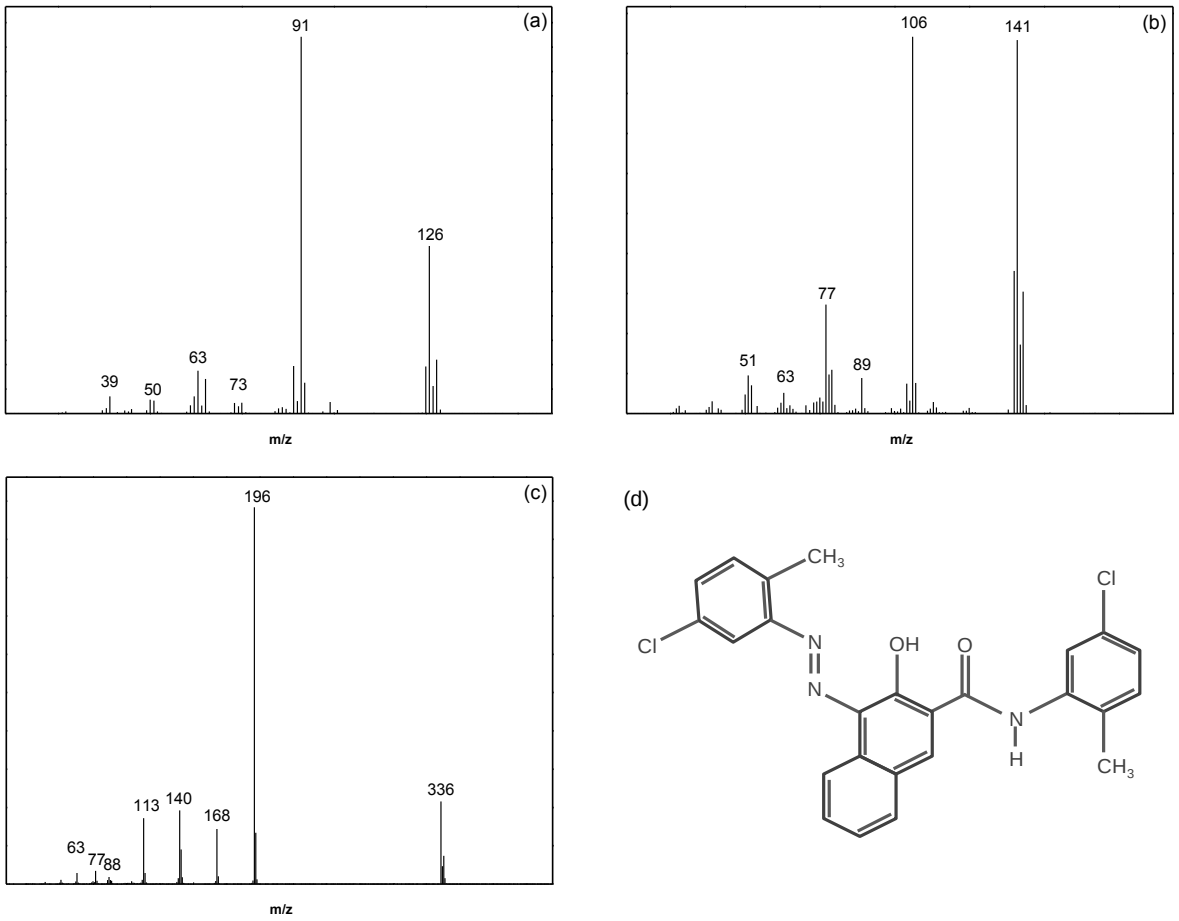

Fig. A3.28: (a)-(c) mass spectrum of the azo red pigment characteristic fractions

(d) Structure of Pigment red 11

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d) Violet

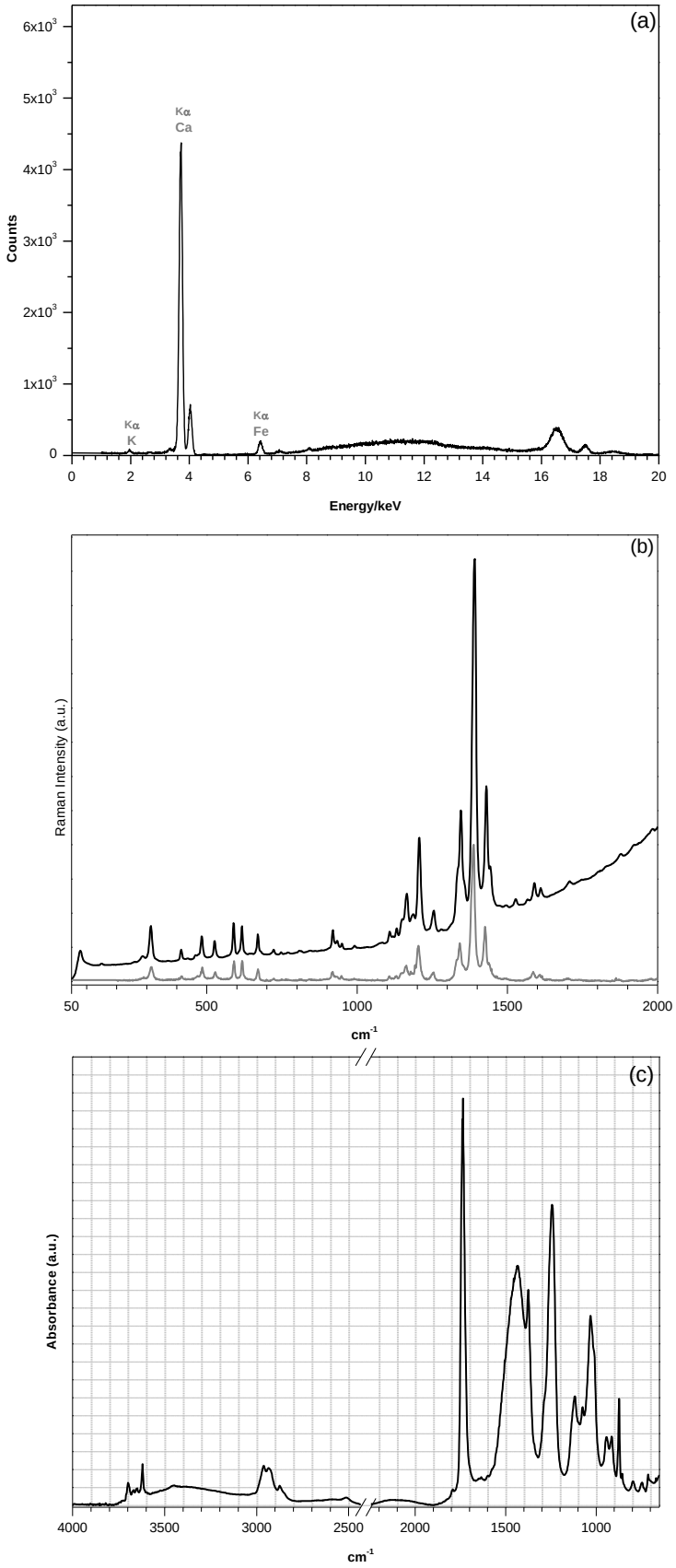


Fig. A3.29: (a) XRF spectrum (b) Raman spectra of *Rowney* violet paint containing an azo pigment (c) Infrared spectra of the PVAc homopolymer binding medium and kaolin

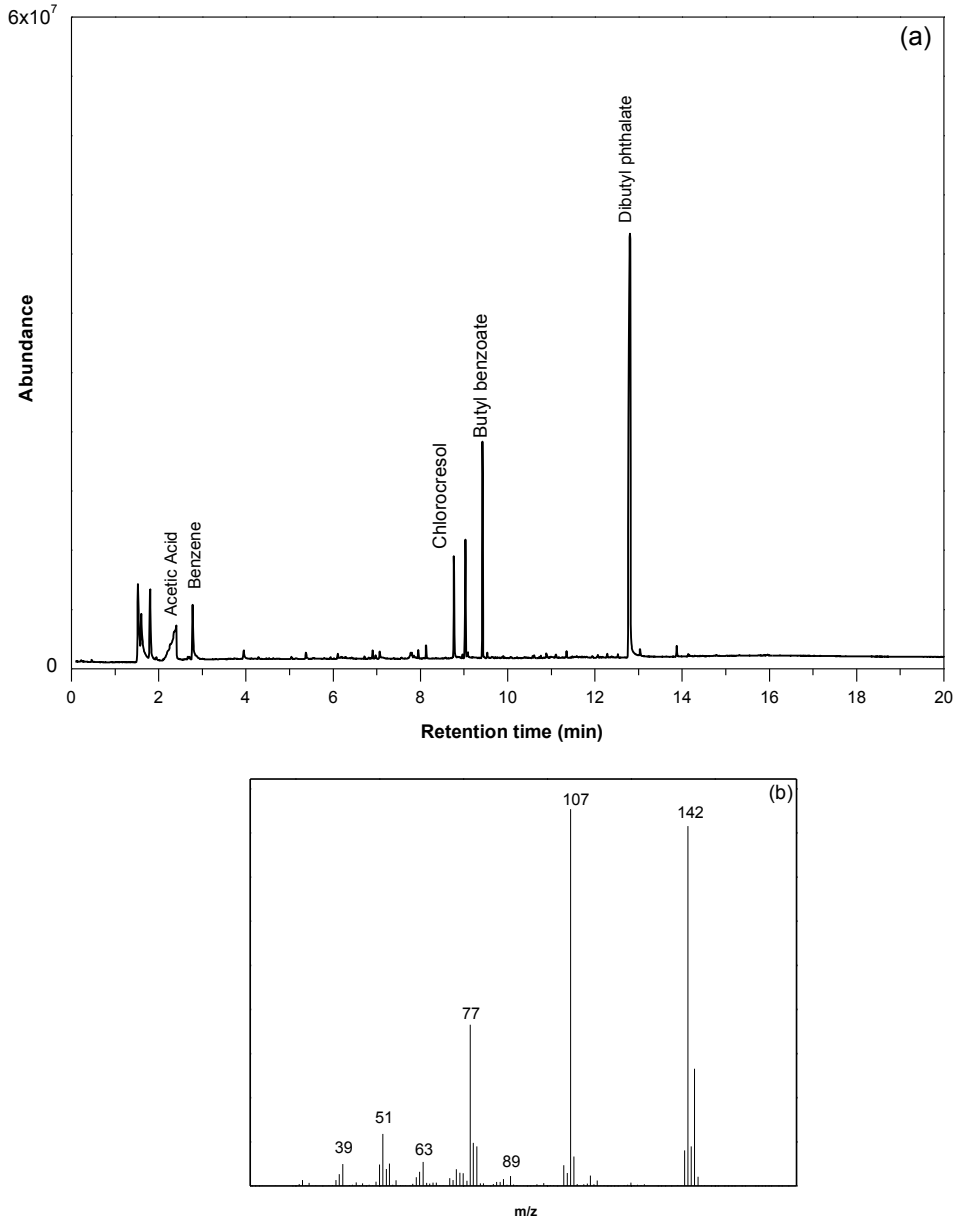


Fig. A3.30: (a) Pyrogram and (b) mass spectrum of the major peak attributed to the violet organic synthetic pigment (peak eluting at 8:77min).

e) Yellow

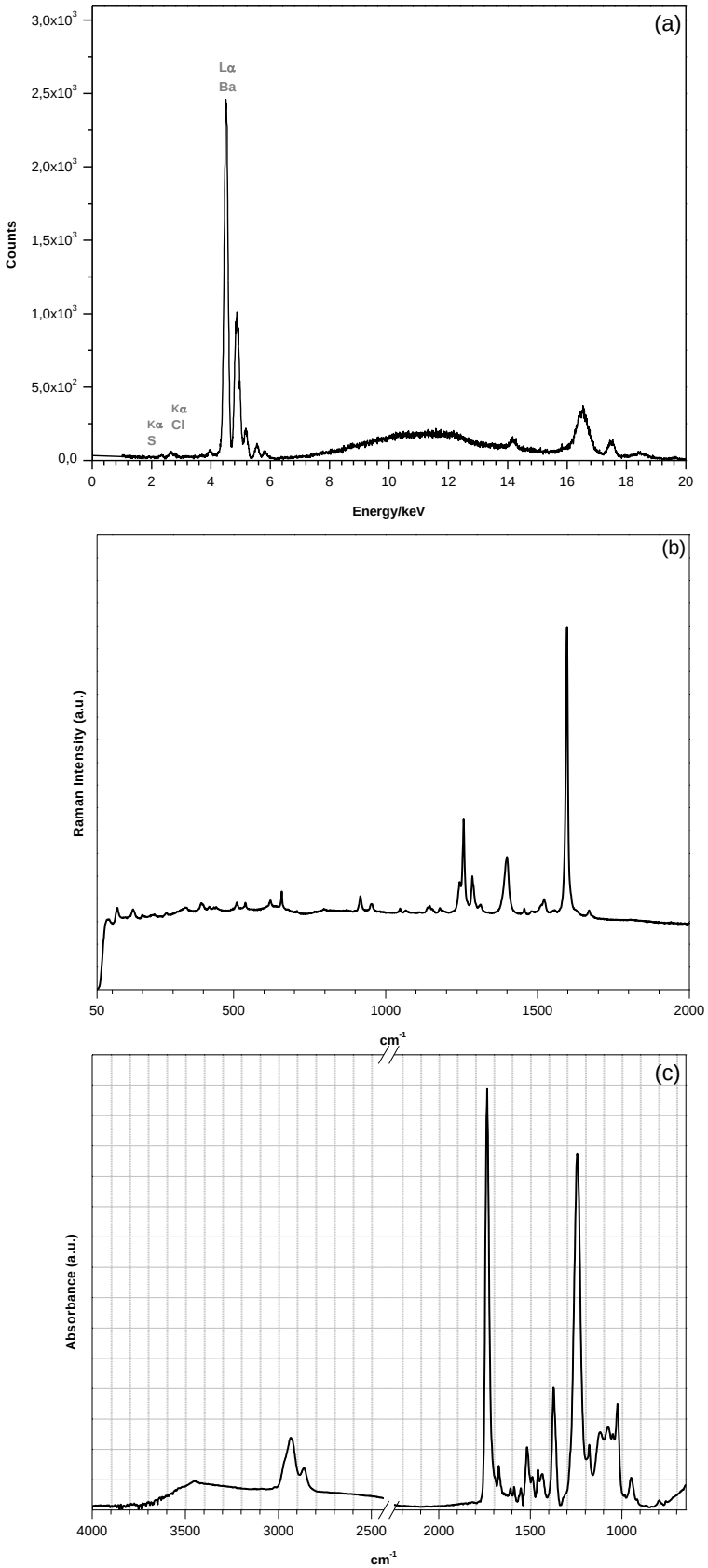


Fig. A3.31: (a) XRF spectrum (b) Raman spectra of *Rowney* yellow paint containing an azo yellow pigment (c) Infrared spectra of the PVAc copolymer binding medium

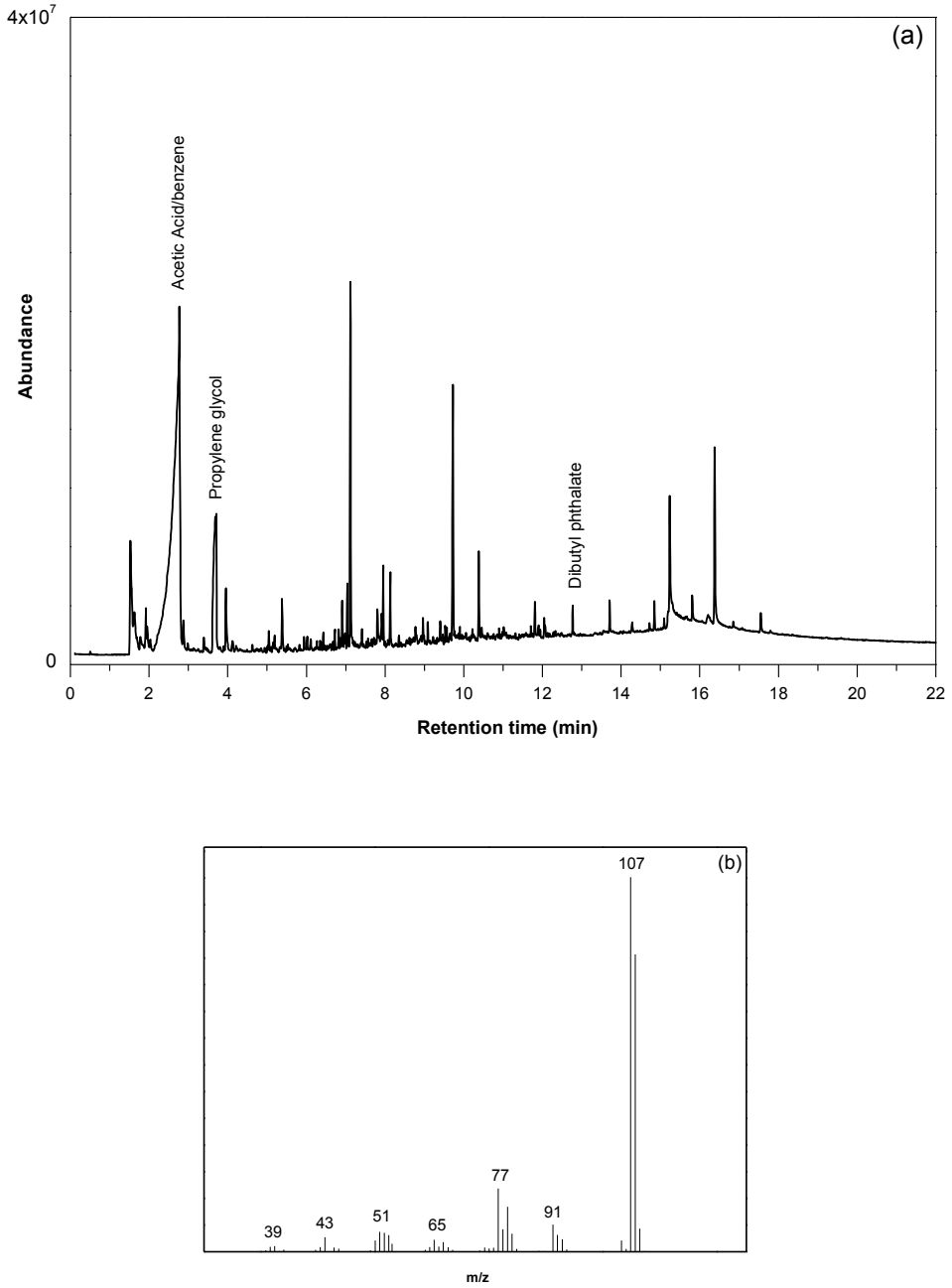


Fig. A3.32: (a) Pyrogram (b) mass spectrum of the major peak from the yellow pigment (peak eluting at 7:12min).

f) White

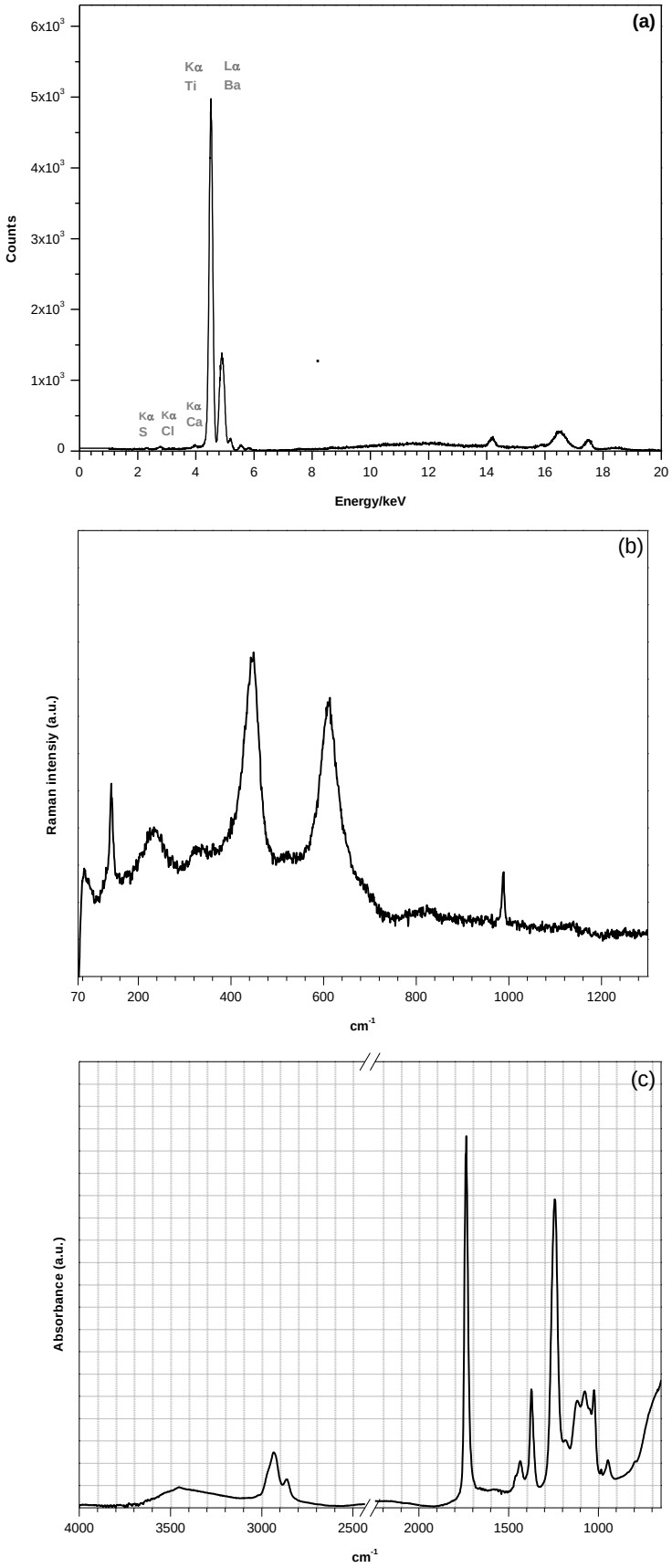


Fig. A3.33: (a) XRF spectrum of *Rowney* white (b) Raman spectra of rutile TiO_2 and $BaSO_4$ (a) Infrared spectrum of the binder containing PVAc and PE

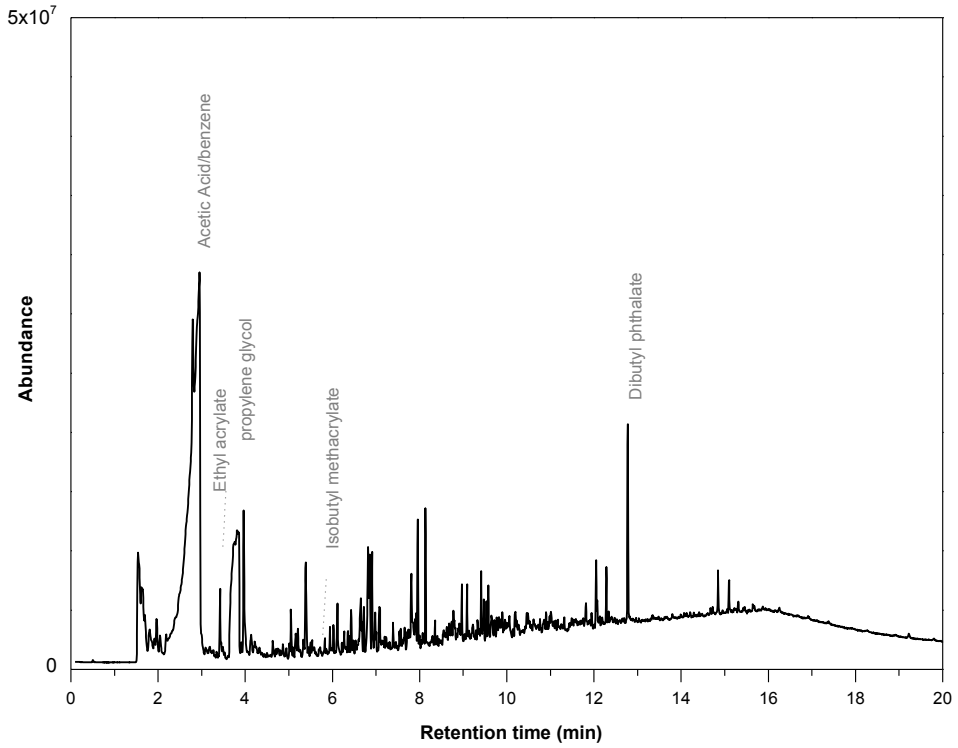


Fig. A3.34: Pyrogram of *Rowney* white.

g) Black

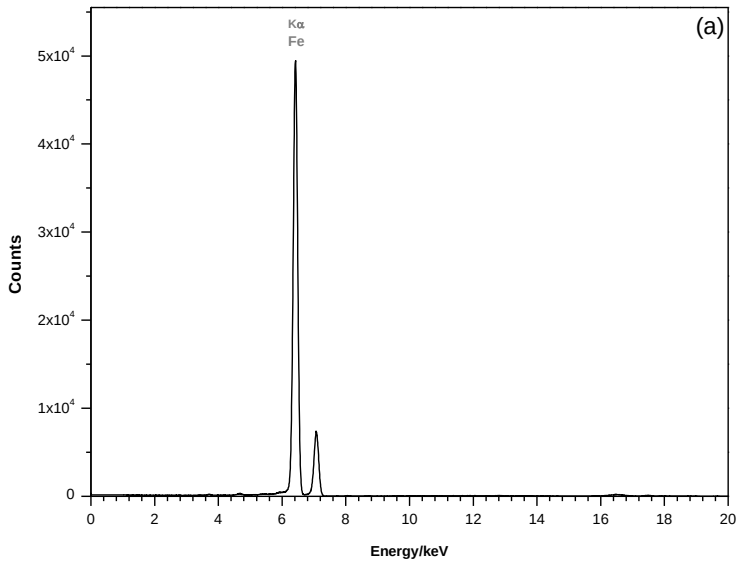


Fig. A3.35: XRF spectrum of *Rowney* black

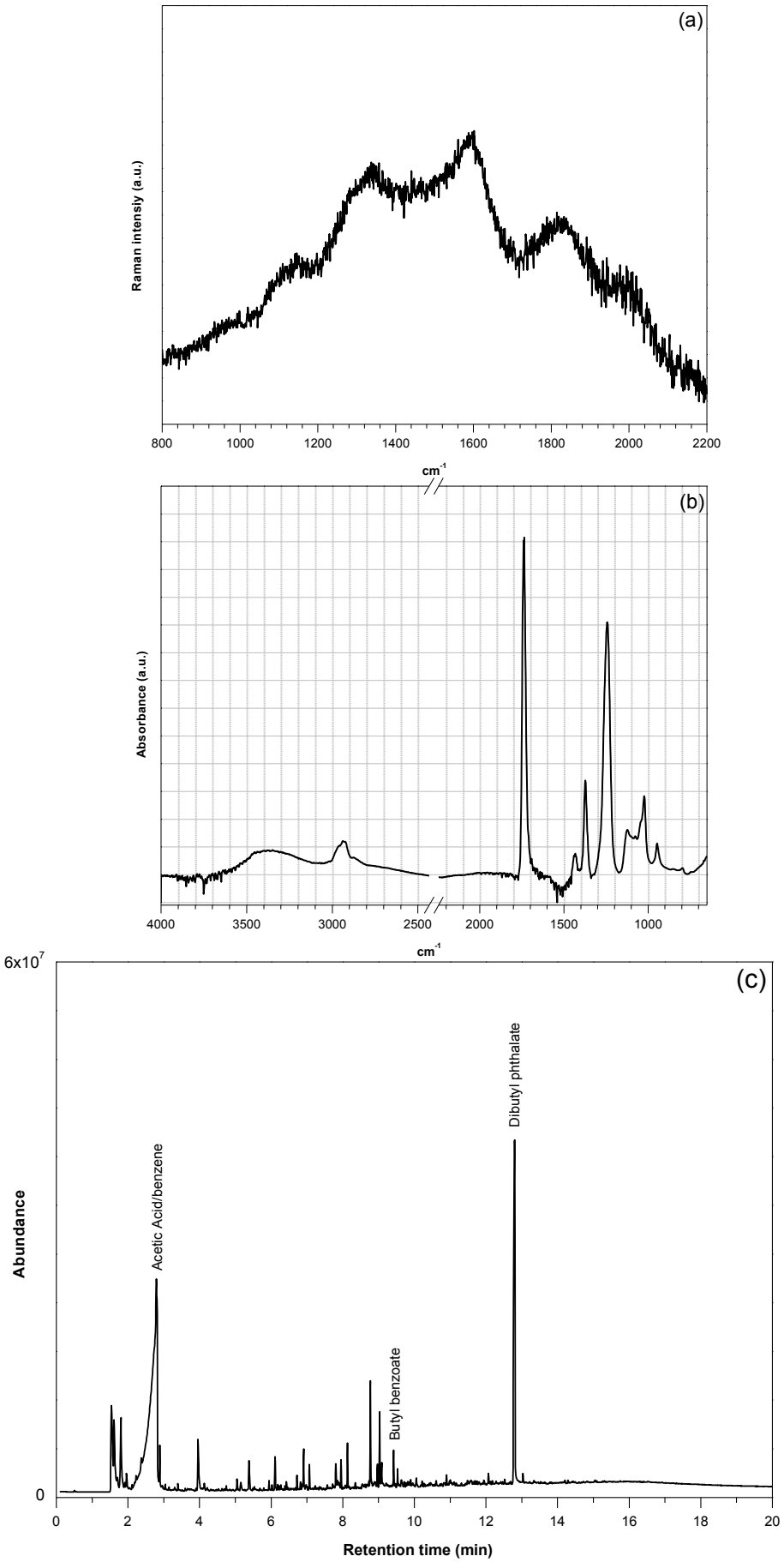


Fig. A3.36: (a) Raman spectra of carbon black (b) Infrared spectrum of the PVAc binding medium of of *Rowney* black (c) Pyrogram.

3.9. Acrylic gypsum Talens

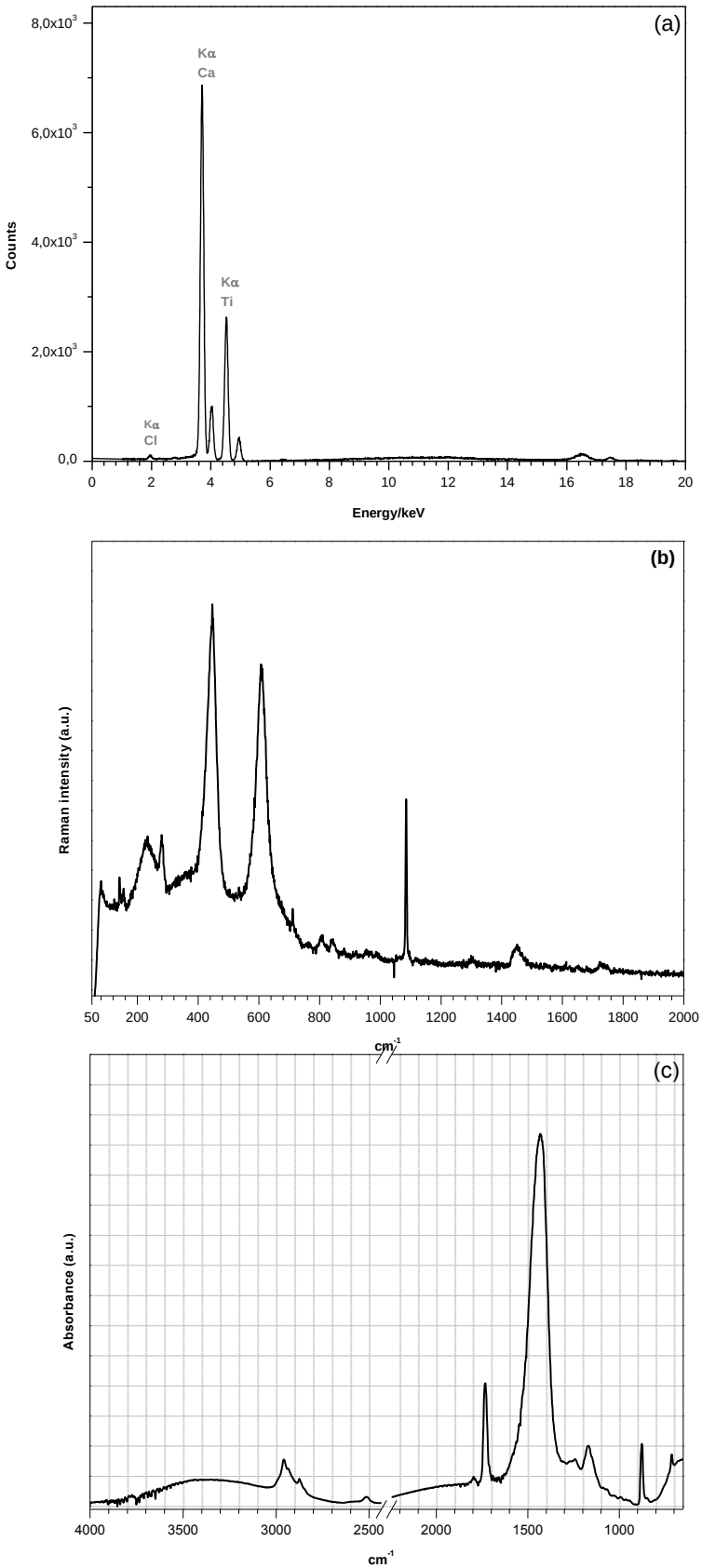


Fig. A3.37: (a) XRF spectrum of the *Talens* acrylic gypsum (b) Raman spectra of rutile TiO_2 and $CaCO_3$ (c) Infrared spectrum of the acrylic binding medium.

Appendix IV: Artificial aging materials and full results

4.1. Materials, aging apparatus and assessment methods

Vulcano V7, the PVAc aqueous emulsion was purchased from *Casa Varela* and *Vinamul 3469* was obtained directly at the Portuguese distributor *Globalcor, S.A.*. The lithopone white and carbon black + iron oxide black pigments were from the *Cenógrafa* brand and were purchased from Casa Varela as ready to use pigments. Titanium white in the rutile form was obtained at the same store. Titanium white in the anatase form and powder poly(methyl methacrylate) (PMMA) were purchased from *Sigma-Aldrich*. Millipore and distilled water were used and the chloroform used was HPLC grade.

Irradiation of the samples was carried out in a SolarBox 3000e (CO•FO•ME•GRA) equipped with a Xenon-arc light source. Molecular changes were followed by infrared spectroscopy in the transmitance and reflectance modes. Alteration of the molecular weight distribution of the polymers was determined with Gel Permeation Chromatography – Size Exclusion Chromatography (GPC-SEC). Color changes were assessed by measuring the Lab* coordinates. Sample weight alterations were measured in order to determine mass loss. The surface's morphology of selected unaged and aged paints was evaluated by Atomic Force Microscopy.

4.2. Weight assessment results

Table A4.1. Differences in weight measured during artificial aging in reproductions done with *Vulcano V7*

Vulcano V7: PVAc homopolymer					
Time	Pure binder	Lithopone + CaCO3	Carbon black +Iron oxide+$CaCO_3$	TiO_2 rutilo	TiO_2 anatase
500h	-7,47%	-0,07%	-0,16%	-0,08%	-0,39%
1750h	-0,17%	-0,15%	-0,20%	-0,14%	-1,00%
3250h	-0,24%	-0,17%	-0,26%	-0,15%	-1,19%
4000h	-0,22%	-0,19%	-0,18%	-0,15%	-1,23%

Table A4.2. Differences in weight measured during artificial aging in reproductions done with *Vinamul 3469*

***Vinamul 3469*: P(VAc-E-VC) terpolymer**					
Time	Pure binder	Lithopone + CaCO3	Carbon black +Iron oxide+$CaCO_3$	TiO_2 rutilo	TiO_2 anatase
500h	-0,22%	-0,02%	-0,02%	-0,01%	-0,78%
1750h	-0,56%	-0,21%	-0,03%	-0,03%	-1,43%
3250h	—	-0,25%	-0,03%	-0,03%	-1,64%
4000h	-0,79%	-0,21%	-0,08%	-0,04%	-1,67%

4.3. Colorimetry results

Table A4.3. L*, a*, b* and ΔE values measured during artificial aging in reproductions done with PVAc homopolymer (*V7*)

***Vulcano V7*: PVAc homopolymer**															
	Pure binder			**Lithopone + $CaCO_3$**			**Carbon black+ Iron oxide+$CaCO_3$**			**TiO_2 rutile**			**TiO_2 anatase**		
	L*	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***
Unaged	89.57	-0.74	5.10	88.54	--1.12	4.30	24.64	0.56	-0.30	95.88	-1.06	3.05	94.51	-0.76	9.72
	±0.06	±0.01	±0.03	±0.05	±0.01	±0.10	±0.04	±0.01	±0.01	±0.02	±0.01	±0.05	±0.02	±0.01	±0.09
500h	89.13	-0.65	5.35	88.17	-1.37	5.94	23.67	0.70	-0.20	95.66	-0.97	1.61	94.15	-0.58	6.64
	±0.62	±0.15	±0.04	±0.20	±0.01	±0.17	±0.03	±0.01	±0.02	±0.01	±0.01	±0.0 2	±0.03	±0.01	±0.17
1750h	88.53	-1.48	9.64	88.28	-1.00	4.19	24.05	0.66	-0.10	95.70	-1.05	2.20	95.56	-0.47	4.47
	±0.01	±0.01	±0.07	±0.05	±0.00	±0.03	±0.01	±0.01	±0.01	±0.13	±0.01	±0.13	±0.11	±0.12	±0.10
3250h	89.18	-1.66	9.36	87.45	-0.82	2.35	24.02	0.67	-0.05	95.69	-1.12	2.75	96.28	-0.16	2.71
	±0.08	±0.01	±0.06	±1.20	±0.02	±0.38	±0.01	±0.01	±0.02	±0.01	±0.01	±0.02	±0.03	±0.02	±0.03
4000h	88.10	-1.32	8.92	89.92	-0.52	4.03	24.15	0.64	-0.16	—	—	—	97.29	-0.59	1.34
	±0.03	±0.01	±0.03	±0.09	±0.02	±0.17	±0.06	±0.02	±0.02				±0.04	±0.02	±0.07
Δ (L*, a*, b*)	**-1.47**	**-0.58**	**3.82**	**1.37**	**0.61**	**-0.27**	**-0.49**	**0.08**	**0.14**	**-0.19**	**1.07**	**-0.30**	**2.78**	**0.17**	**-8.38**
ΔE		**4.14**			**1.53**			**0.51**			**1.12**			**8.83**	

Table A4.4. L*, a*, b* and ΔE values measured during artificial aging in reproductions done with P(VAc-E-VC) terpolymer (*Vinamul 3469*)

***Vinamul 3469*: P(VAc-E-VC) terpolymer**															
	Pure binder			**Lithopone + $CaCO_3$**			**Carbon black+ iron oxide+$CaCO_3$**			**TiO_2 rutile**			**TiO_2 anatase**		
	L*	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***
Unaged	89.16	-1.02	4.82	89.96	-0.77	1.93	25.21	0.61	0.12	92.04	-0.98	2.49	95.50	-0.92	1.64
	±0.18	±0.01	±0.03	±0.04	±0.01	±0.04	±0.10	±0.03	±0.02	±0.15	±0.01	±0.10	±0.02	±0.01	±0.03
500h	76.13	4.51	52.22	86.17	-1.12	11.41	24.80	0.69	0.31	95.69	0.03	1.31	95.46	-0.95	2.53
	±0.12	±0.07	±0.32	±1.12	±0.17	±2.38	±0.03	±0.01	±0.01	±0.01	±0.01	±0.01	±0.10	±0.01	±0.03
1750h	71.00	7.96	55.74	73.85	3.99	19.93	25.06	0.72	0.45	96.65	-0.06	1.14	93.87	-1.28	5.48
	±0.17	±0.14	±0.41	±0.12	±0.03	±0.02	±0.04	±0.03	±0.03	±0.01	±0.01	±0.02	±0.02	±0.01	±0.03
3250h	67.13	8.37	45.86	70.73	4.95	17.94	24.27	0.73	0.49	96.75	-0.09	1.41	92.01	-0.64	13.41
	±0.14	±0.21	±0.77	±0.01	±0.01	±0.07	±0.02	±0.01	±0.01	±0.01	±0.01	±0.01	±0.11	±0.04	±0.13
4000h	68.37	8.40	49.91	73.05	4.01	17.89	23.19	0.89	0.24	96.77	-0.25	1.40	91.51	0.43	14.76
	±0.52	±0.69	±3.16	±0.02	±0.01	±0.02	±0.02	±0.01	±0.03	±0.02	±0.02	±0.02	±0.08	±0.03	±0.05
Δ (L*, a*, b*)	**-22.03**	**1.23**	**41.04**	**-16.91**	**4.78**	**15.97**	**-2.02**	**0.28**	**-0.12**	**4.73**	**0.73**	**-1.09**	**-3.49**	**0.96**	**11.76**
ΔE		**46.59**			**23.74**			**2.04**			**4,91**			**12,31**	

4.4. FTIR results of artificial aging of *Vulcano V7* and *Vinamul 3469*

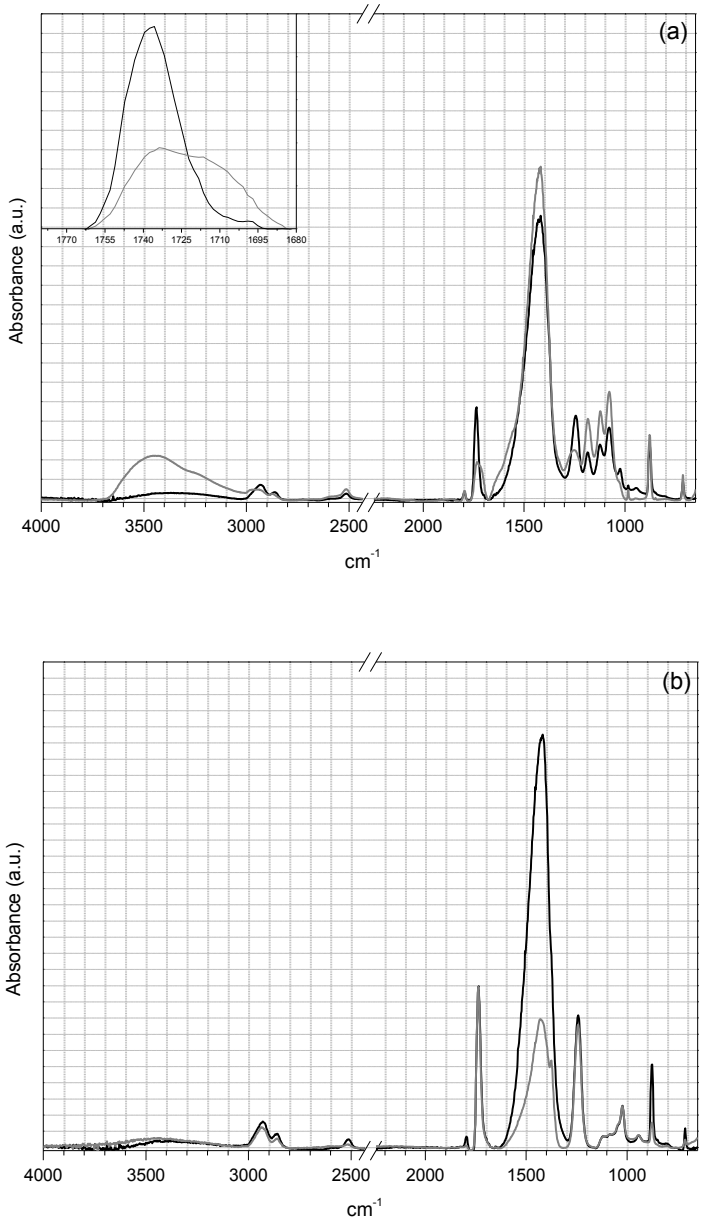


Fig. A4.1. Infrared spectra obtained with diamond cell of the pigmented samples containing the *Vinamul* emulsion and (a) *Cenógrafa* white (b) *Cenógrafa* black at time 0 (—) and after 4000h (—) of Xenon irradiation. The white and black paint samples show that the distribution of the $CaCO_3$ was heterogeneous.

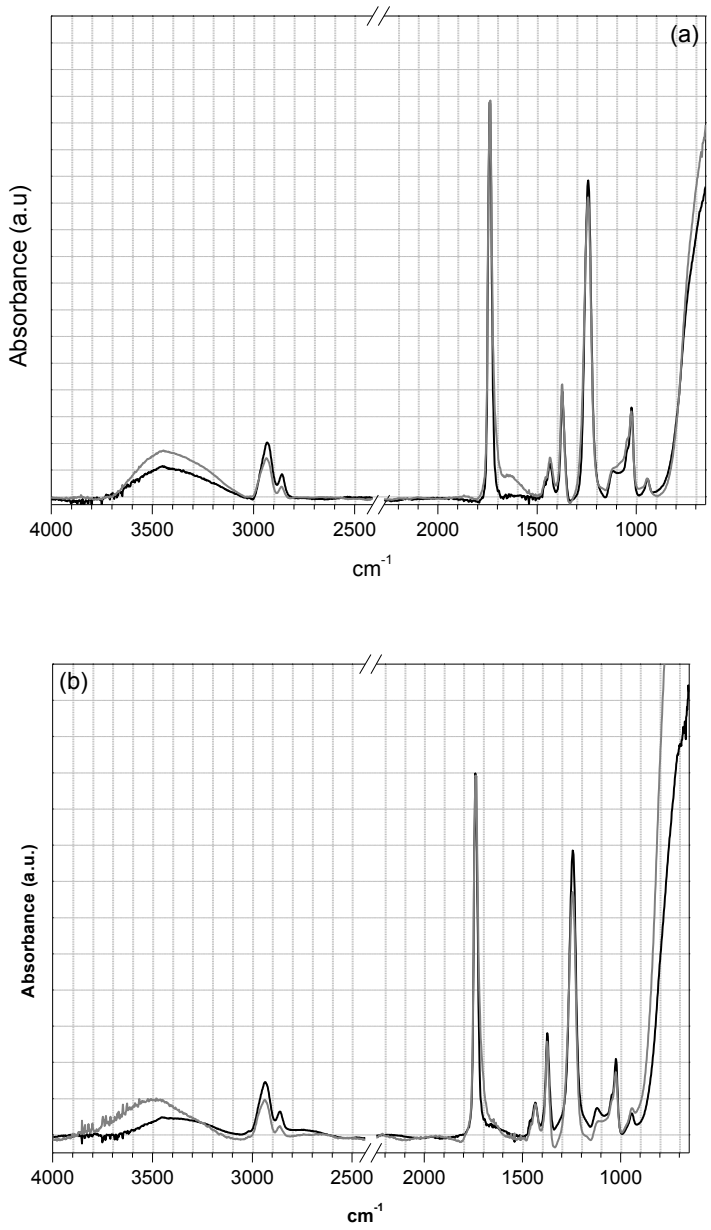
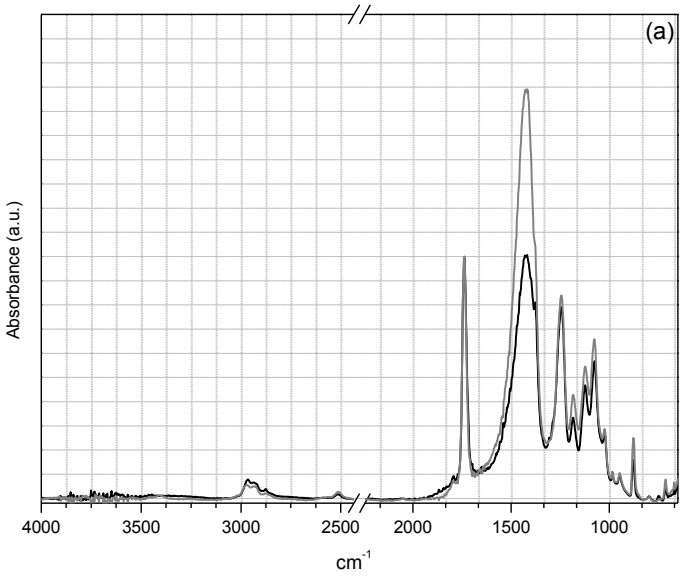


Fig. A4.2. Infrared spectra obtained with diamond cell of the pigmented samples containing the *Vinamul* emulsion and (a) TiO_2 rutile (b) and TiO_2 anatase at time 0 (—) and after 4000h (—) of Xenon irradiation.

Table A4.5. Relative intensity of the main infrared absorptions in the infrared spectra of the terpolymer *Vinamul* normalized for the C=O stretching. Infrared spectra were baseline corrected. Before and after 4000h of artificial aging.

	νC-H		**νC=O**	**δC-H (CH_2)**	**δC-H (CH_3)**	**νC-O (CO)O**	**νC-C**	**ν C-O O(CH)**
	2934-36	**2860-62**	**1733-36**	**1432-35**	**1372-75**	**1233-42**	**1116-20**	**1022-24**
Vinamul unaged	0,25 ±0,08	0,11 ±0,04	1,00	0,18 ±0,05	0,47 ±0,12	0,96 ±0,07	0,22 ±0,09	0,49 ±0,17
Vinamul aged	*0,17 ±0,04*	*0,07 ±0,02*	*1,00*	*0,13 ±0,2*	*0,35 ±0,06*	*0,86 ±0,11*	*0,15 ±0,04*	*0,34 ±0,08*
***Vinamul* + litopone unaged**	0,15 ±0,00	0,07 ±0,01	1,00	$CaCO_3$		0,92 ±0,03	$BaSO_4$	0,34 ±0,04
Vinamul + litopone aged	*0,12 ±0,01*	*0,07 ±0,03*	*1,00*			*1,21 ±0,14*		*0,41 ±0,14*
***Vinamul* + black unaged**	0,14 ±0,01	0,07 ±0,01	1,00	$CaCO_3$		0,79 ±0,03	0,06 ±0,00	0,23 ±0,00
Vinamul + black aged	*0,12 ±0,00*	*0,06 ±0,00*	*1,00*			*0,74 ±0,01*	*0,07 ±0,01*	*0,25 ±0,02*
***Vinamul* + TiO_2 rutile unaged**	0,13 ±0,01	0,06 ±0,00	1,00	0,08 ±0,01	0,26 ±0,02	0,77 ±0,03	0,08 ±0,03	0,22 ±0,02
Vinamul+ TiO_2 rutile aged	*0,10 ±0,02*	*0,03 ±0,01*	*1,00*	*0,11 ±0,03*	*0,29 ±0,03*	*0,76 ±0,00*	*0,09 ±0,02*	*0,22 ±0,01*
***Vinamul* + TiO_2 anatase unaged**	0,14 ±0,00	0,06 ±0,00	1,00	0,09 ±0,01	0,29 ±0,01	0,81 ±0,01	0,08 ±0,03	0,23 ±0,02
Vinamul + TiO_2 anatase aged	*0,07 ±0,02*	*0,07 ±0,02*	*1,00*	*0,10 ±0,02*	*0,36 ±0,00*	*0,79 ±0,07*	*0,13 ±0,07*	*0,35 ±0,15*



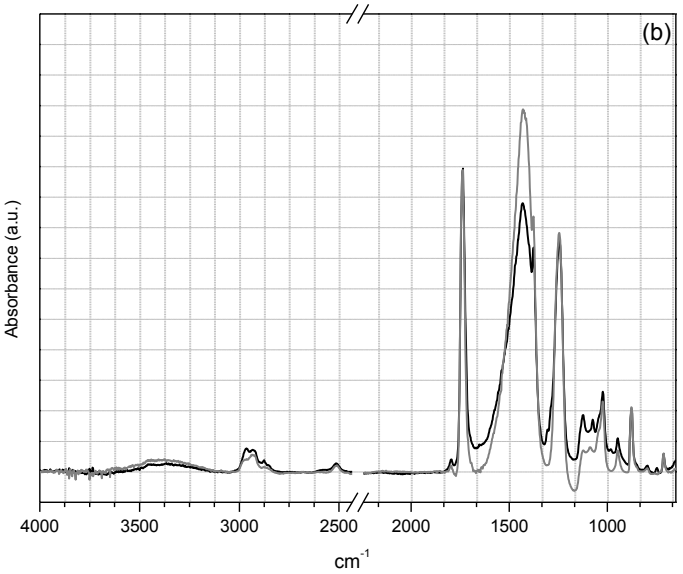


Fig. A4.3. Infrared spectra of the pigmented samples containing the *V7* emulsion and (a) *Cenógrafa* white (b) *Cenógrafa* black pigment at time 0 (—) and after 4000h (—) of Xenon irradiation. The white and black paint samples show that the distribution of the $CaCO_3$ was heterogeneous.

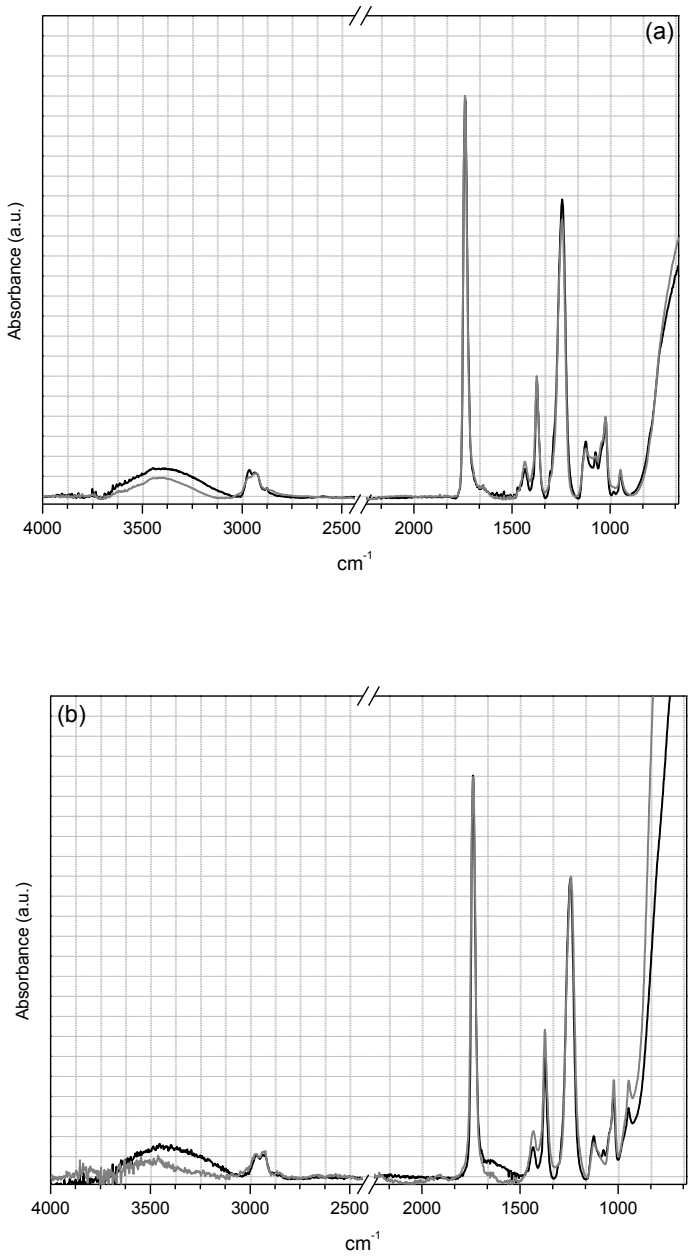


Fig. A4.4. Infrared spectra of the pigmented samples containing the *V7* emulsion and (a) TiO_2 rutile (b) and TiO_2 anatase at time 0 (—) and after 4000h (—) of Xenon irradiation.

Table A4.6: Relative intensity of the main infrared absorptions in the infrared spectra of the *V7* homopolymer normalized for the C=O stretching before and after 4000h of artificial aging.
Infrared spectra were baseline corrected.

	νC-H (influenced by DiBP)			**νC=O**	**δC-H (CH_2)**	**δ C-H(CH_3)**	**ν C-O (CO)O**	**δ (ring-H) (DiBP)**	**ν C-O (C-O-CO) (DiBP)**	**ν C-O O(CH)**
	2965	2937	**2876**	**1736**	1432	**1373**	1241	**1123**	**1073**	1022
***V7* unaged**	0,09 ±0,01	0,08 ±0,01	0,03 ±0,00	1,00	0,09 ±0,01	0,34 ±0,05	0,81 ±0,07	0,20 ±0,04	0,17 ±0,03	0,27 ±0,04
V7 aged	*0,07 ±0,02*	*0,06 ±0,01*	*0,02 ±0,00*	*1,00*	*0,08 ±0,01*	*0,31 ±0,06*	*0,75 ±0,11*	*0,16 ±0,03*	*0,13 ±0,03*	*0,24 ±0,06*
***V7* + litopone unaged**	0,09 ±0,02	0,07 ±0,02	0,04 ±0,02	1,00	$CaCO_3$		0,80 ±0,05	$BaSO_4$		0,24 ±0,04
V7* + *litopone aged	*0,07 ±0,02*	*0,06 ±0,02*	*0,03 ±0,02*	*1,00*			*0,86 ±0,02*			*0,26 ±0,02*
***V7* + black unaged**	0,07 ±0,01	0,07 ±0,01	0,03 ±0,01	1,00	$CaCO_3$		0,75 ±0,04	0,16 ±0,02	0,15 ±0,02	0,26 ±0,03
V7* + *black aged	*0,04 ±0,01*	*0,05 ±0,01*	*0,01 ±0,01*	*1,00*			*0,78 ±0,06*	*0,11 ±0,02*	*0,11 ±0,02*	*0,26 ±0,03*
***V7* + TiO_2 rutile unaged**	0,07 ±0,00	0,06 ±0,00	0,02 ±0,01	1,00	0,06 ±0,00	0,28 ±0,01	0,71 ±0,02	0,13 ±0,01	0,11 ±0,01	0,18 ±0,01
V7* + *TiO_2 rutile aged	*0,05 ±0,01*	*0,05 ±0,01*	*0,01 ±0,01*	*1,00*	*0,09 ±0,01*	*0,30 ±0,02*	*0,70 ±0,01*	*0,13 ±0,01*	*0,11 ±0,01*	*0,20 ±0,01*
***V7* + TiO_2 anatase unaged**	0,06 ±0,02	0,06 ±0,01	0,04 ±0,04	1,00	0,07 ±0,01	0,30 ±0,01	0,75 ±0,02	0,12 ±0,01	0,09 ±0,03	0,23 ±0,06
V7* + *TiO_2 anatase aged	*0,08 ±0,03*	*0,08 ±0,02*	—	*1,00*	*0,12 ±0,03*	*0,32 ±0,02*	*0,78 ±0,05*	*0,12 ±0,05*	—	*0,30 ±0,13*

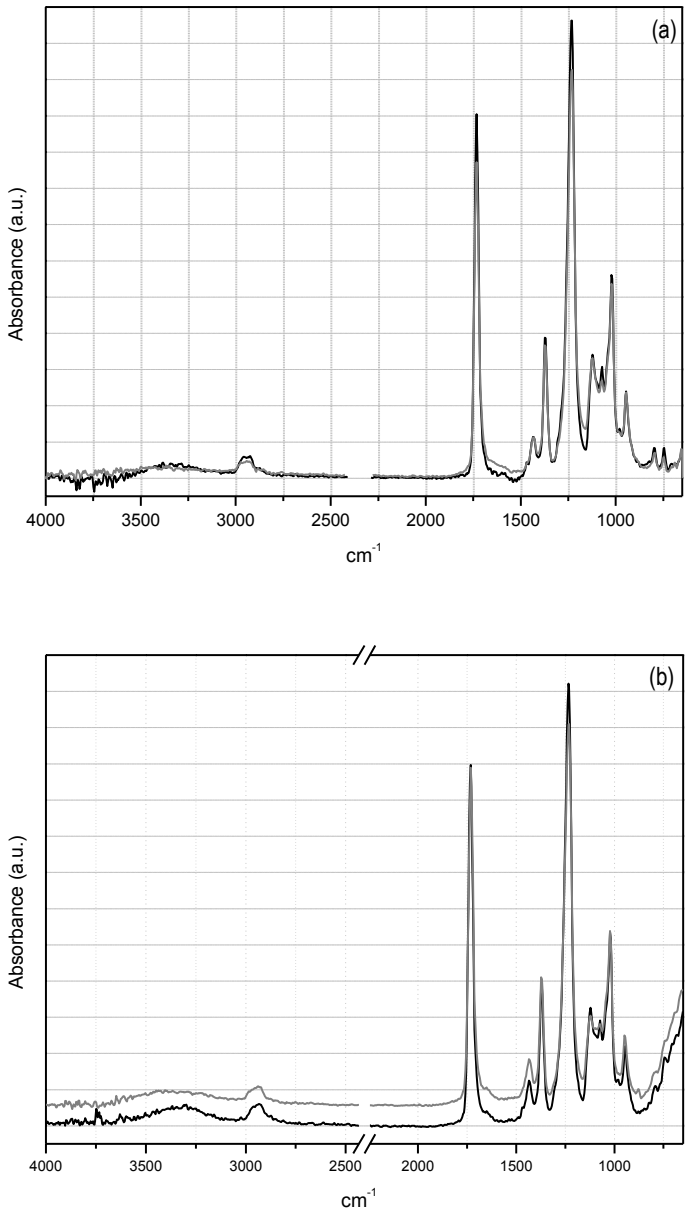


Fig. A4.5 ATR infrared spectra of the pure (a) *V7* emulsion sample and (b) pigmented with TiO_2 rutile at time 0 (—) and after 4000h (—) of Xenon irradiation.

Table A4.7 – Infrared absorptions in ATR normalized for the C=O stretching before and after artificially aging.

	νC-H	νC-H	νC-H	νC=O	δC-H (CH_2)	δC-H(CH_3)	νC-O (CO)O	νC-C	νC-C	ν C-O O(CH)
***V7* unaged**	**2961-51**	**2933-31**	**2888-74**	**1736-31**	**1436-30**	**1373**	**1234**	**1124-21**	**1073**	**1022**
	—	**—**	**—**	1.00	0.14 ±0.00	0.41 ± 0.00	1.22 ±0.01	0.31 ±0.00	0.28 ±0.01	0.58 ±0.01
V7 aged 5000h	***2984-73***	***2940-33***	***2899-48***	***1733-31***	***1436-33***	***1373-71***	***1234-33***	***1124-21***	***1076-73***	***1022***
	—	**—**	**—**	*1.00*	*0.16 ±0.02*	*0.41 ± 0.01*	*1.19 ±0.05*	*0.30 ±0.01*	*0.28 ±0.01*	*0.57 ±0.01*
***V7* unaged**	**2961-51**	**2933-31**	**2888-74**	**1736-31**	**1436-30**	**1373**	**1234**	**1124-21**	**1073**	**1022**
	0.06 ±0.00	0.06 ±0.00	**—**	1.00	0.11 ±0.01	0.38 ± 0.00	1.25 ±0.02	0.34 ±0.01	0.30 ±0.01	0.55 ±0.01
V7 aged 3250h	***2984-73***	***2940-33***	***2899-48***	***1733-31***	***1436-33***	***1373-71***	***1234-33***	***1124-21***	***1076-73***	***1022***
	0.05 ±0.00	*0.05 ±0.00*	**—**	*1.00*	*0.14 ±0.01*	*0.40 ± 0.01*	*1.25 ±0.03*	*0.33 ±0.04*	*0.29 ±0.02*	*0.59 ±0.02*
***V7* + rutile unaged**	**2961-51**	**2933-31**	**2888-74**	**1736-31**	**1436-30**	**1373**	**1234**	**1124-21**	**1073**	**1022**
	0.06 ±0.01	0.07 ±0.01	0,03 ±0.00	1.00	0.13 ±0.01	0.41 ± 0.00	1.29 ±0.00	0.35 ±0.01	0.33 ±0.01	0.60 ±0.01
V7 + rutile aged	***2984-73***	***2940-33***	***2899-48***	***1733-31***	***1436-33***	***1373-71***	***1234-33***	***1124-21***	***1076-73***	***1022***
	0.12 ±0.01	*0.13 ±0.01*	*0,10 ±0.00*	*1.00*	*0.22 ±0.01*	*0.44 ± 0.00*	*1.13 ±0.00*	*0.32 ±0.01*	*0.31 ±0.01*	*0.57 ±0.01*
***V7* + litopone unaged**	**2970-62**	**2940-30**	—	**1734**	**1433**	**1373**	**1234-33**	**1124-18**	**1076-73**	**1022**
	—	**—**	**—**	1.00	**—**	**—**	1.26 ±0.10	**—**	**—**	**—**
V7 + litopone aged	***2965-56***	***2931-25****	—	***1734***	***1433***	***1373***	***1234-32***	***1124-21***	***1073***	***1022***
	—	**—**	**—**	*1.00*	**—**	**—**	*1.26 ±0.10*	**—**	**—**	**—**
***V7* + negro unaged**	**2961-51**	**2933-31**	**2888-74**	**1736-31**	**1436-30**	**1373**	**1234**	**1124-21**	**1073**	**1022**
				1.00	**—**	**—**	1.21 ±0.10	0.57 ±0.02	0.56 ±0.01	0.80 ±0.01
V7 + negro aged	***2984-73***	***2940-33***	***2899-48***	***1733-31***	***1436-33***	***1373-71***	***1234-33***	***1124-21***	***1076-73***	***1022***
	—	**—**	**—**	*1.00*	**—**	**—**	*1.22 ±0.08*	*0.74 ±0.08*	**—**	*0.93 ±0.05*

Vinamul in Si wafers

Polymer photodegradation was also followed in Si wafers to extend the spectral window to the characteristic absorption bands of carbon-chlorine stretching vibrations at 640 and 620 cm^{-1} but the results are not discussed because a plausible explanation for what was observed could not be found. In this case, contrary to what was observed in the glass slides the degradation resulted in strong spectral changes (Fig A4.5) leading to the formation of new bands; in the hydroxyl region at c.3433cm^{-1} and 3234cm^{-1}; in the C-H stretching window, at 2966cm^{-1} and 2941cm^{-1} together with a decrease of the C-H absorptions at 2876cm^{-1} and 2861cm^{-1} (present in the unaged terpolymer). Formation of a band at c. 1634cm^{-1} can be correlated with double conjugated bonds [48] and the observed yellowing of the terpolymer. The appearance of a band at 1168cm^{-1} could be related to the C-O stretching in the OH group of hydroxyl/hydroperoxy groups that shows up in the 1200-1000cm^{-1} region [9]. Moreover formation of a band at 1046cm^{-1} in the aged sample could not be attributed as no reference was found in the literature. The carbonyl absorption broadens, the absorption of the initial band at c.1735cm^{-1} decreases, and a shoulder appears at 1778cm^{-1}. This band could be attributed to the formation of ketones. [48] The vC-O band at 1240cm^{-1} also broadens.

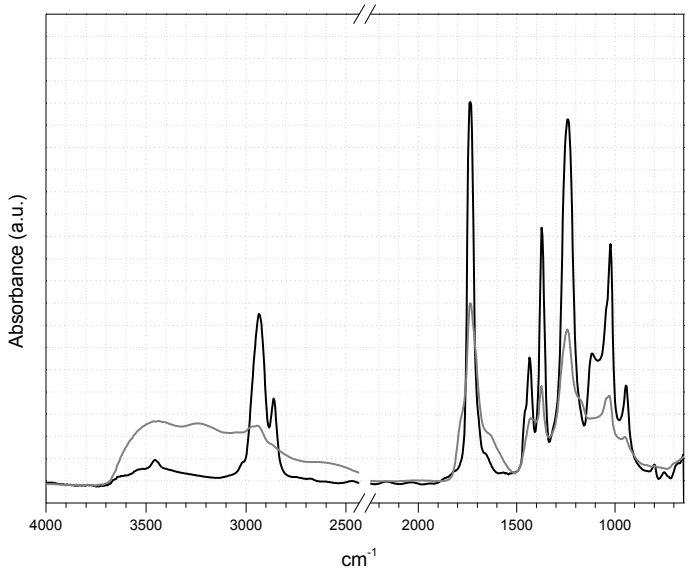


Figure A4.6: Infrared spectra of the *Vinamul* emulsion on silicon disks at time 0 (—) and after 4000h (—) of artificial aging

4.5. GPC-SEC results for artificial aging of *Vulcano V7* and *Vinamul 3469*

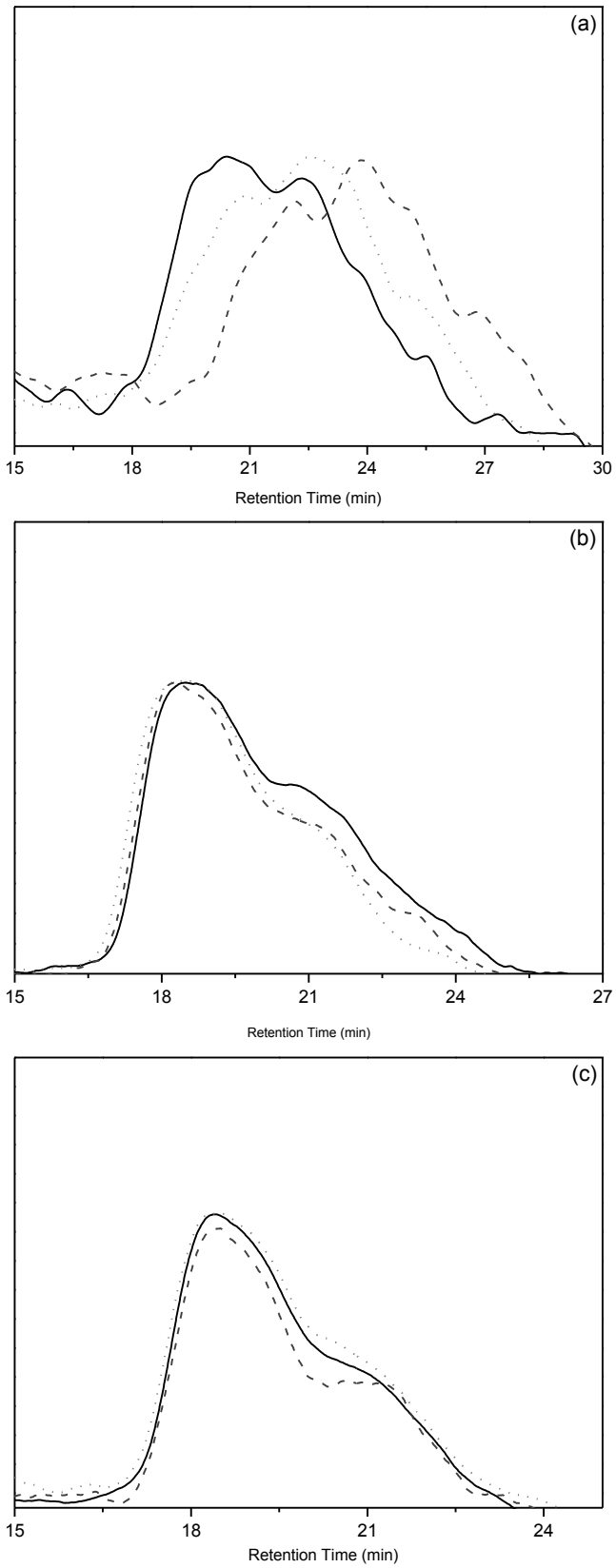


Fig. A4.7. Molecular weight distribution over irradiation time for *V7* and (a) lithopone (b), rutile (c) anatase (—)0 h; (- - -) 1750h; (····) 4000h.

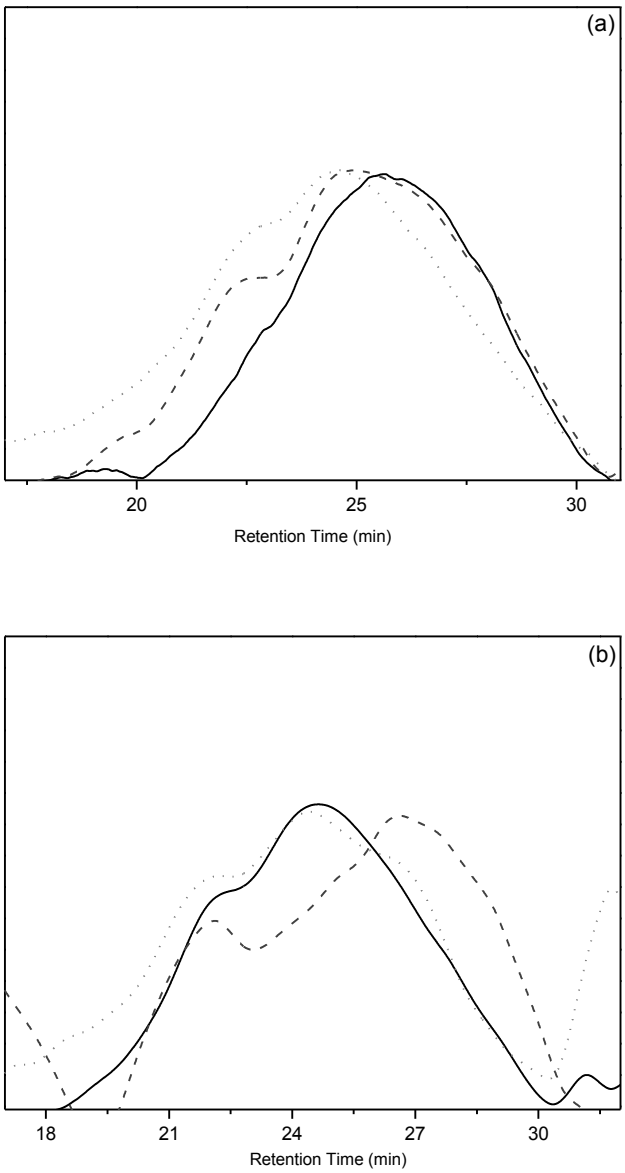


Fig. A4.8. Molecular weight distribution over irradiation time for *Vinamul* (a) and TiO_2 rutile (b) and TiO_2 anatase : (—)0 h; (- - -) 1750h; (····) 4000h.

4.6. Py-GC/MS results for artificial aging of *Vulcano V7* (PVAc homopolymer)

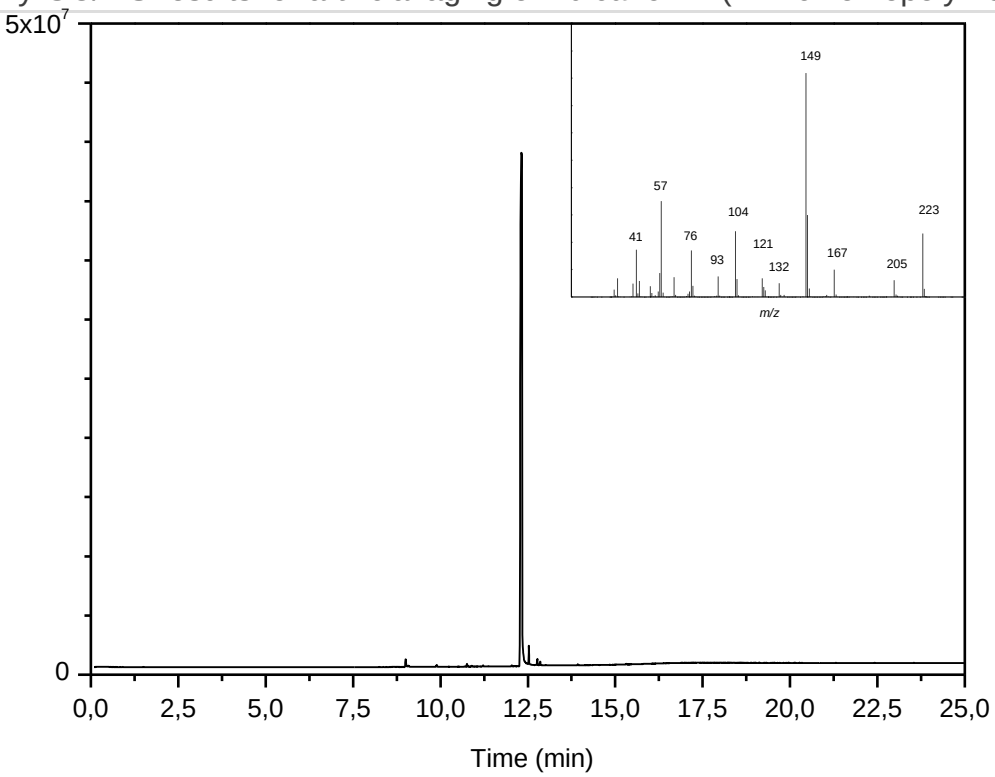


Fig. A4.9. Pyrogram between 100-225ºC of the *Vulcano V7* unaged only containing DiBP plasticizer (peak eluting at c. 12:37min) (mass spectrum shown in inlay).

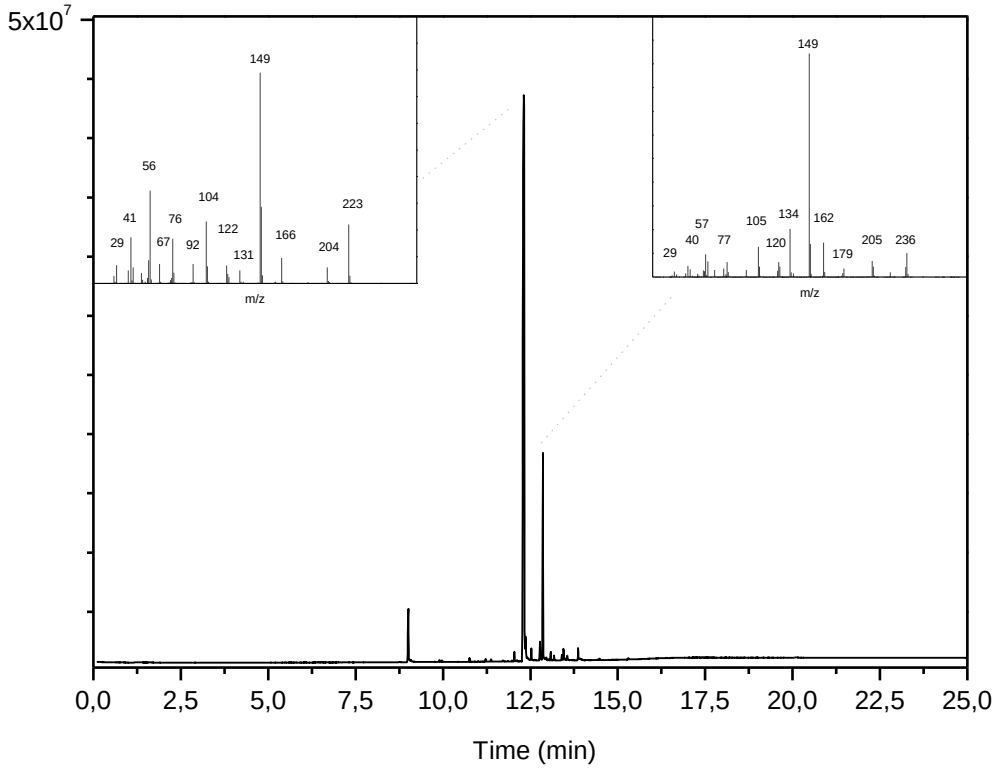


Fig. A4.10. Pyrogram between 100-225ºC of the *Vulcano V7* aged containing DiBP plasticizer (peak eluting at c.12:37min and mass spectrum shown in inlay on the left) and a peak of 1-2-benzene carboxylic acid (or, phthalic anyhride) (peak eluting at c.12:84 and mass spectrum shown on inlay on the right) probably related to phthalate degradation.

Table A4. 8: Molecular species produced on the pyrolysis of the unaged sample of *Vulcano V7*, the corresponding retention time, molecular weight and m/z values.

Molecular species	Retention time	Mw	m/z
Carbon dioxide	1:50	44	44
Water	1:53	18	18
E-butene	1:58	56	56,41,39,27
Acetone	1:76	58	58,43
1-3-cyclopentadiene	1:93	66	66,39
Acetic Acid	2:71	60	60,43,45
Benzene	2:75	78	78, 51
Toluene	3:94	92	91,65
styrene	5:37	104	104,78,51
2-propenyl benzene	6:72	118	117
Indene	6:90	116	116, 89
acetophenone	7:01	120	120,105,77
1,2 - dihydronaphthalene	7:81	130	129,115
1,4 - dihydronaphthalene	7:95	130	130,115
naphthalene	8:13	128	128
1-methyl-naphthalene	8:97	142	142,115
Isobutyl benzoate	9:11	178	123,77,105
biphenyl	9:53	154	154, 76
Diisobutyl phthalate	12:32	149	149,223, 57, 104
butyl isobutyl ester phthalic acid	12:53	278	149

Table A4. 9: Molecular species produced on the pyrolysis of the *Vulcano V7* sample artificially aged for 4000h, the corresponding retention time, molecular weight and m/z values.

Molecular species	**Retention time**	**Mw**	**m/z**
Carbon dioxide	1:52	44	44
Water	1:60		
1-3-cyclopentadiene	1:95	66	66,39
Acetic Acid	2:77	60	60,43
Benzene	2:78	78	78, 51
Toluene	3:95	92	91,65
styrene	5:39	104	104,78,51
Benzaldehyde	6:08	120	105,77,51
1-propenyl benzene	6:72	118	117,91
Indene	6:91	116	116, 89
acetophenone	7:07	120	105,77,120,51
1,4 - dihydronaphthalene	7:81	130	130,115
1,2 - dihydronaphthalene	7:95	130	129,115
naphthalene	8:13	128	128
1-methyl-naphthalene	8:97	142	142,115
Isobutyl benzoate	9:10	178	123,77,105
biphenyl	9:53	154	154, 76
Diisobutyl phthalate	12:32	149	149,223, 57, 104
Isobutyl 2-methylallyl ester phthalic acid	12:37	276	149,55,104,132
Dibutyl phthalate	12:53	278	149
...phthalate	12:78	278	149,205,57,104
Butyl neopentyl ester phthalic acid	12:86	292	149,132,162,104,57
2-methylbutyl pentyl ester phthalic acid	13:08	306	149,57,71,41,104

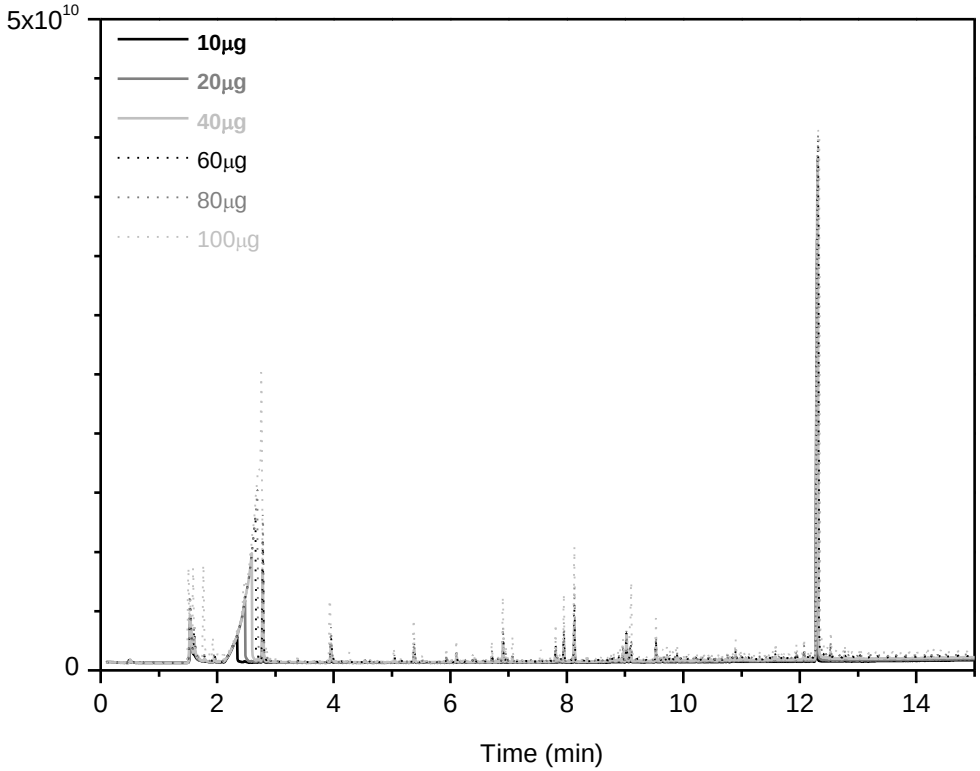


Fig. A4.11. Pyrogram used for quantification by Py-GC/MS of the phthalate content in the unaged sample of *Vulcano V7*

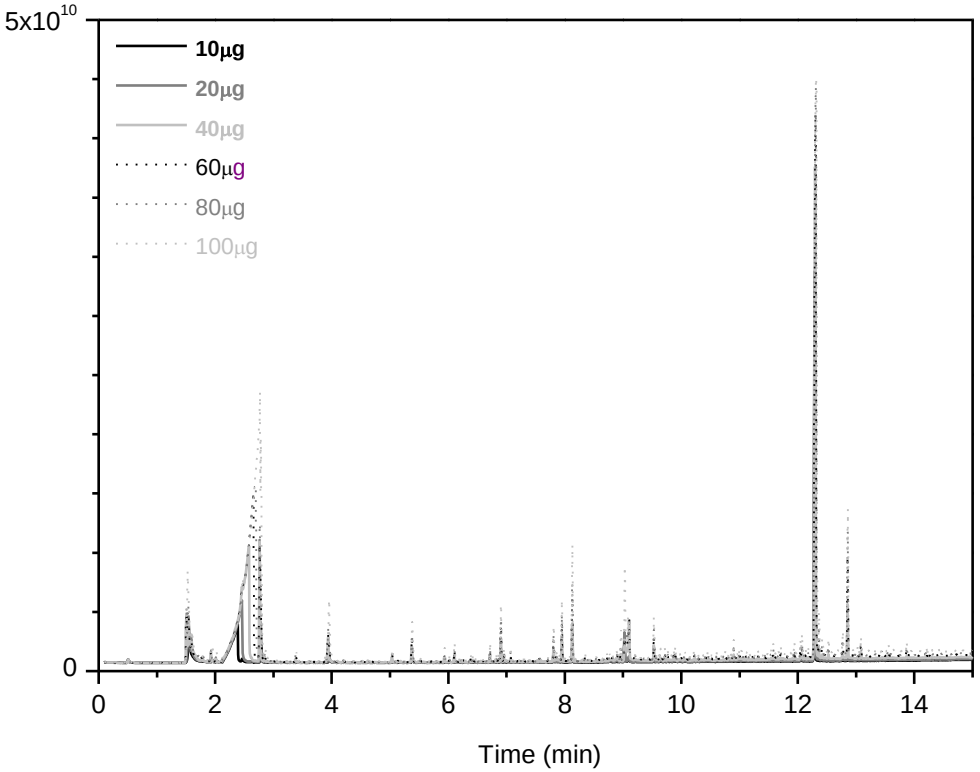


Fig. A4.12. Pyrograms used for quantification by Py-GC/MS of the phthalate content in the 4000h artificially aged sample of *Vulcano V7*

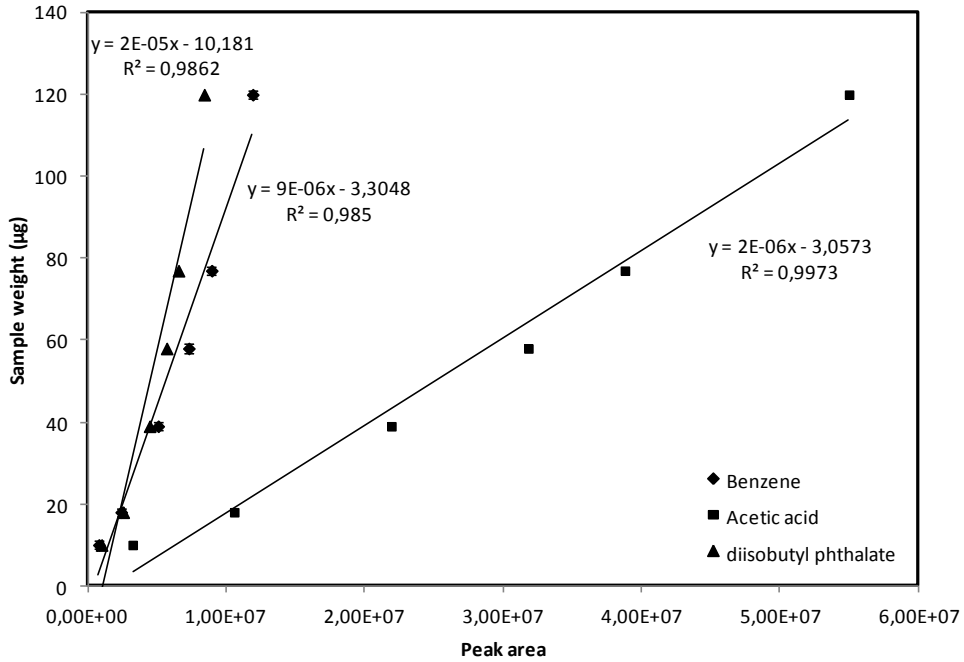


Fig. A4.13. Calibration curves used for quantification by Py-GC/MS of the phthalate content in unaged sample of *Vulcano V7*. Integration of the peaks for the ion 60 for acetic acid, ion 78 for benzene and ion 149 for the phthalate were used for the calculation of the peak areas.

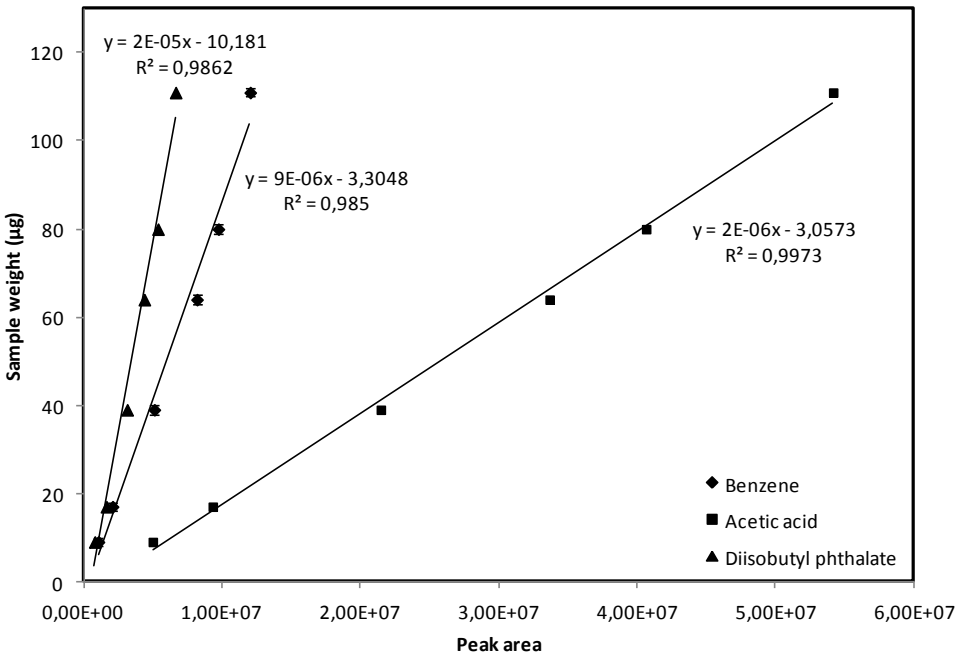


Fig. A4.14. Calibration curves used for quantification by Py-GC/MS of the phthalate content in the artificially aged of *Vulcano V7* (4000h). Integration of the peaks for the ion 60 for acetic acid, ion 78 for benzene and ion 104 for the phthalates were used for the calculation of the peak areas.

Table A4.10. Estimation of the ratios between acetic acid and phthalates in the *Vulcano V7* without aging. Peak areas were calculated through the Integration of the peaks for the ion 60 for acetic acid, ion 78 for benzene and ion 104 for the phthalates in the unaged *Vulcano V7*.

***V7*_unaged**					
Sample weight (µg)	**Peak areas (x10^5)**			**Ratios**	
	Benzene	**Acetic Acid**	**Phthalates**	**Benzene/ Acetic acid**	**Phthalates/ Acetic acid**
100	119	550	84	22	15
80	89	388	65	23	17
60	73	318	57	23	18
40	51	219	45	23	20
20	24	106	25	23	24
10	8	32	9	24	30
			Average	**23**	**21**
			STDV	**1**	**6**

Table A4.11. Estimation of the ratios between acetic acid and phthalates in the aged *Vulcano V7* (4000h). Peak areas were calculated through the Integration of the peaks for the ion 60 for acetic acid, ion 78 for benzene and ion 104 for the phthalates.

***V7*_artificially aged for 4000h**					
Sample weight (µg)	**Peak areas (x10^5)**			**Ratios**	
	Benzene	**Acetic Acid**	**Phthalates**	**Benzene/ Acetic acid**	**Phthalates/ Acetic acid**
100	120	542	66	22	12
80	97	407	54	24	13
60	82	337	44	24	13
40	51	215	31	24	15
20	21	93	16	22	17
10	11	50	79	21	16
			Average	**23**	**14**
			STDV	**1**	**2**

Quantification of the composition of *Vinamul 3469*

Table A4.12. Final results of the ratio estimation between acetic acid and phthalates in the unaged and aged *Vulcano V7* (4000h) and the PVC content on the unaged *Vinamul 3469*.

Sample	**Composition**	**Result**
Vinamul 3469	PVAc+PVC	16% of PVC
***Vulcano V7* unaged**	PVAc + Dibutyl phthalate	23% of benzene to acetic acid
		21% of additives to acetic acid
***Vulcano V7* aged**	PVAc + Dibutyl phthalate + a not identified phthalate (maybe due to degradation of the additive)	23% of benzene to acetic acid
		14% of additives to acetic acid

4.7. TGA and DSC results

For the Thermal Gravimetric Analysis (TGA) the following remarks can be taken. In the case of the terpolymer the absence of additives explains why there is only one curve for weight loss until 400ºC. For the *Vulcano V7* the aged sample starts to lose weight earlier (160ºC) than the unaged sample (200ºC). Probably due to chain scission that occurred in the aged sample. In the aged sample there seems to be less plasticizer to be liberated with heat probably because the sample loss the additive during ageing. For the pigmented sample of *Vulcano V7* height loss in the aged sample seems to be related to loss of plasticizer and polymer, on the double shot in the Py-GC/MS the analysis done between 100ºC-225ºC there is plasticizer and polymer being released.

Table A4.13 – Summary of results obtained with TGA analysis.

Sample	Polymer +additive	Results
***Vinamul* unaged**	P(VAc–E-VC) No additive	Height loss between: 115ºC to 390ºC - 61%
***Vinamul* aged**	P(VAc-E-VC) No additive	Height loss between: 115ºC to 390ºC - 58%
***V7* unaged**	PVAc + diisobutyl phthalate	Height loss between: 120ºC to 250ºC - 19%
***V7* aged**	PVAc+ + diisobutyl phthalate + non identified phthalate	Height loss between: 120ºC to 250ºC - 15%
***V7* + lithopone unaged**	PVAc + diisobutyl phthalate	Height loss between: 100ºC to 250ºC - 5%
***V7* + lithopone aged**	PVAc+ + diisobutyl phthalate + non identified phthalate	Height loss between: 100ºC to 250ºC - 3%
White paint sample from the 90's	PVAc + dibutyl phthalate	Height loss between: 100ºC to 250ºC - 6%

Table A4.14 – Summary of results obtained with DSC analysis.

Sample	Polymer +addittive	Results
***Vinamul* unaged**	P(VAc-E-VC)	15.2 ºC
***Vinamul* aged**	P(VAc-E-VC)	18.2 ºC
***V7* unaged**	PVAc + DiBP	10.2 ºC
***V7* aged**	PVAc + DiBP + phthalate	20.0 ºC
***V7* + lithopone unaged**	PVAc + DiBP	16.2 ºC
***V7* + lithopone aged**	PVAc + DiBP + phthalate	21.4 ºC
White paint sample from the 90's	PVAc + Dibutylphthalate	14.9 ºC
Bizonte	PVAc + Diethylene glycol dibenzoate	10.3 ºC
Imofan AV44/11	PVAc- VeoVa	21.5 ºC

Appendix V: Case studies full results

5.1 *Cinquenta dois (Dez quadros para o ano 2000),* 1985 (MCB)

Fig. A5.1: Scheme with the location of the removed samples

Table A5.1: Summary of analytical results of *Cinquenta e dois (Dez quadros para o ano 2000)*

	Colour	Composition
S1	Black paint layer	PVAc + carbon black, $BaSO_4$, TiO_2 (rutile and traces of anatase), kaolin
S2	Red paint layer	PVAc + hematite (Fe_2O_3), TiO_2 (rutile and probably some traces of anatase), kaolin
S3	White/yellowish paint layer	PVAc + TiO_2 (anatase), barium sulphate, $CaCO_3$; carbon black
S4	White paint layer	PVAc + TiO_2 (anatase), $BaSO_4$, $CaCO_3$
S5	Yellow paint layer	PVAc + lithopone, $CaCO_3$

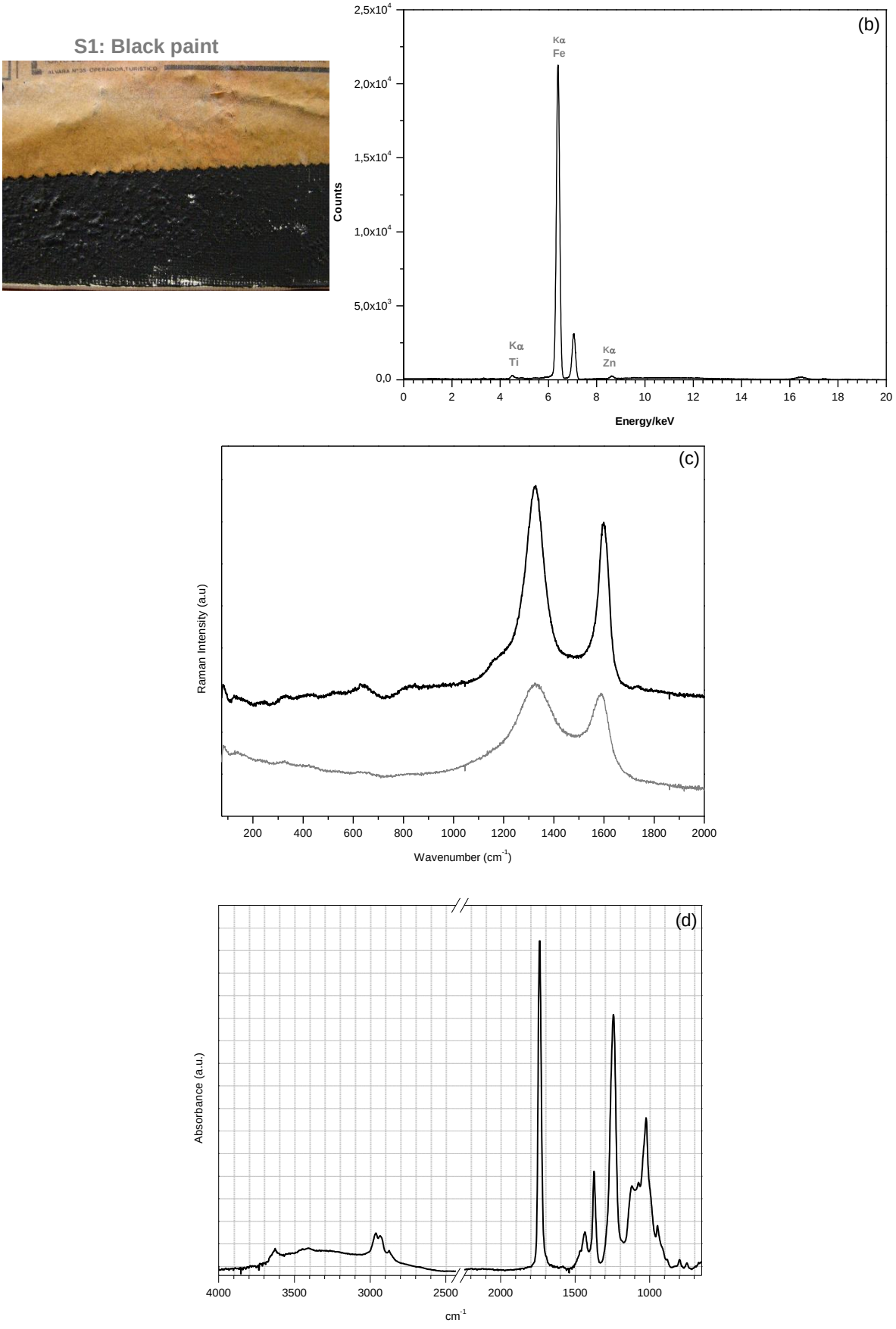


Fig. A5.2: (a) Detail of the surface (b) XRF spectrum (c) Raman spectrum of carbon black in the paint sample (—) and reference spectra (—) (d) FTIR spectra of the vinyl based binder and kaolin.

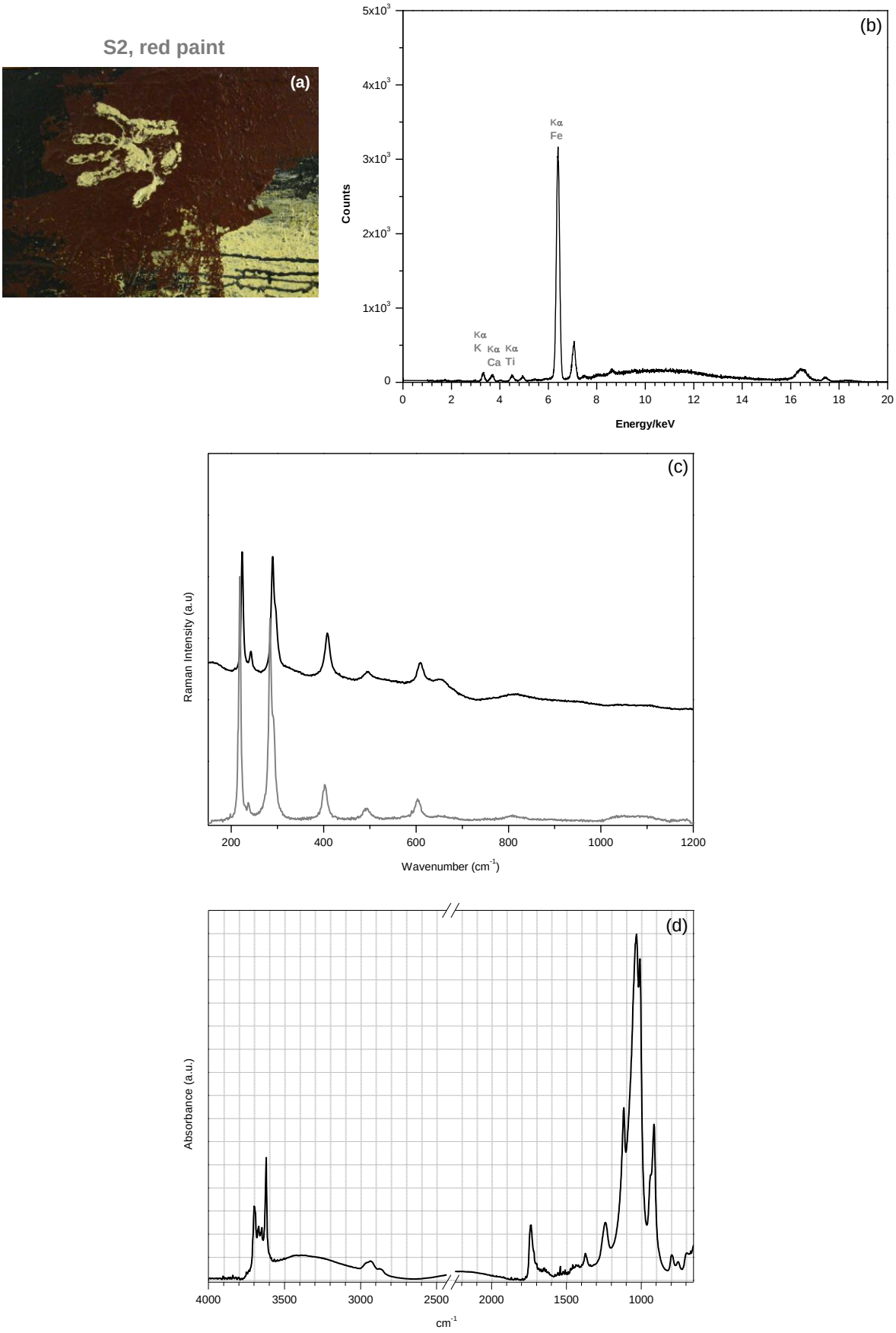


Fig.A5.3: (a) Detail of the red paint (b) XRF spectrum (c) Raman spectra from the sample (—) red iron oxide (—) reference spectra of Fe_2O_3 (d) FTIR spectra of the vinyl based binder and kaolin.

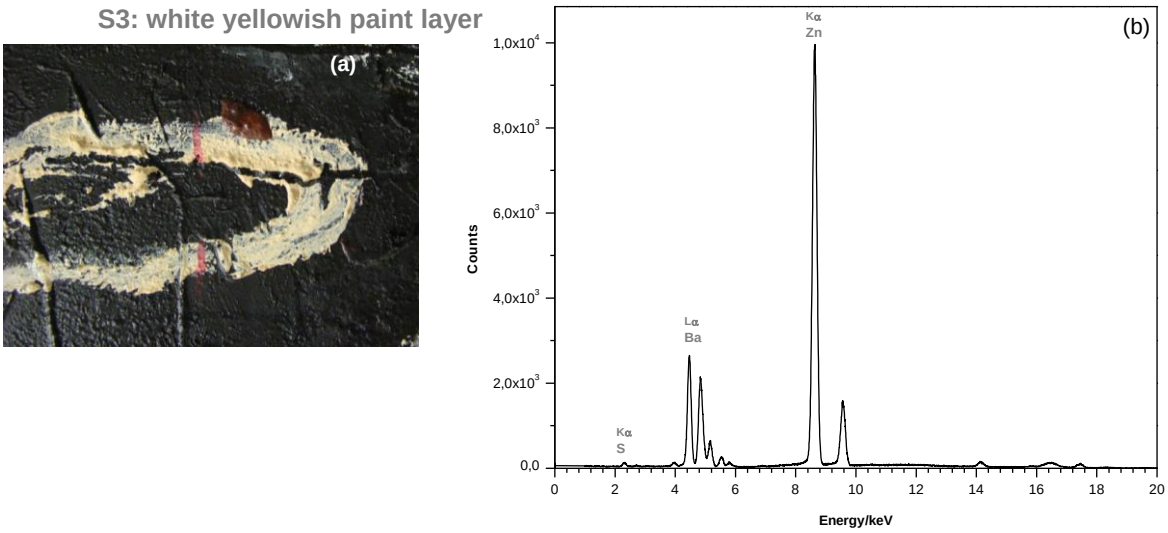


Fig.A5.4: (a) Detail of the white/yellowish paint (b) XRF spectrim from the sample.

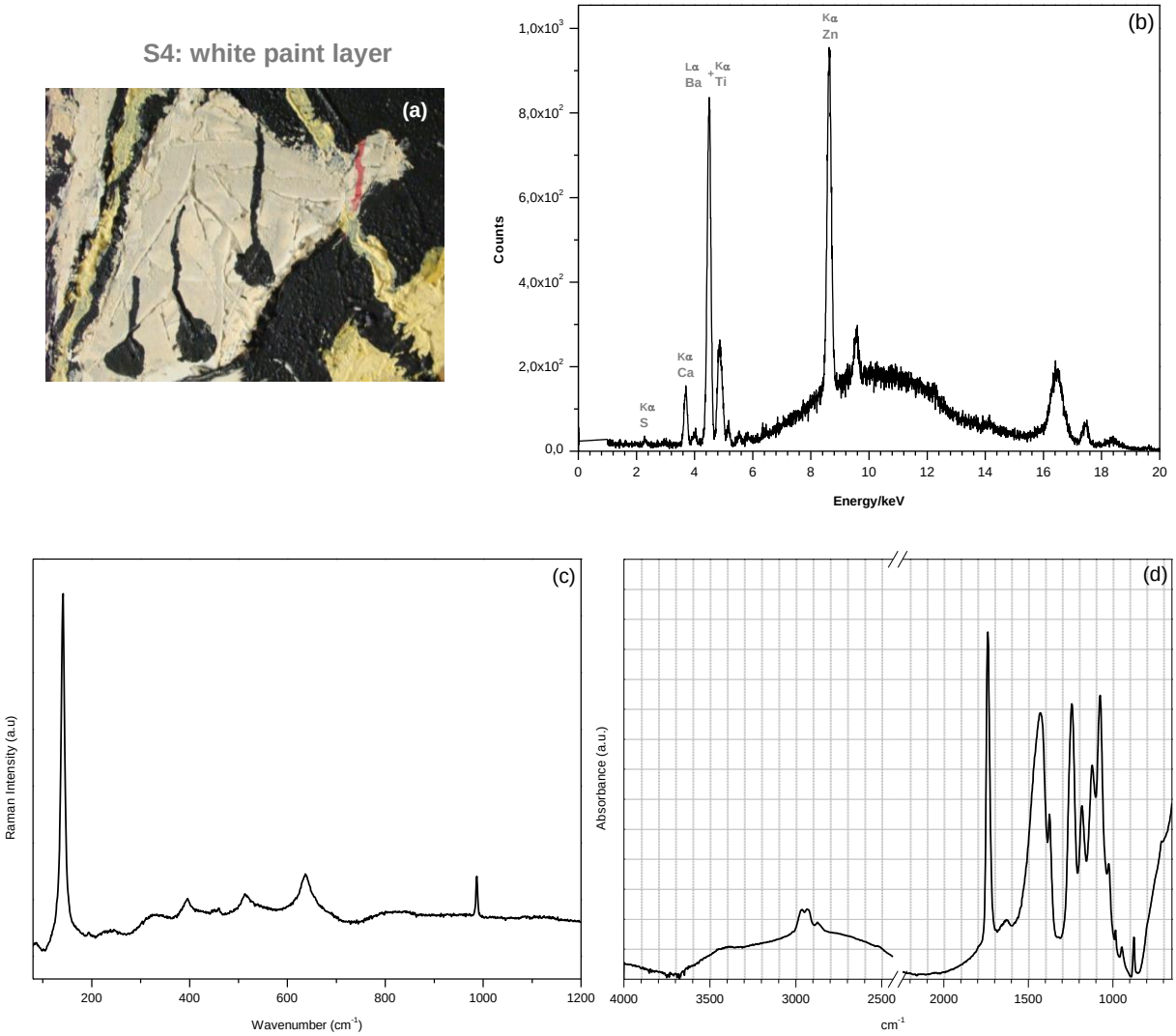


Fig. A5.5: (a) Detail of the paint layer (b) XRF spectrum (c) Raman spectrum from the white anatase TiO_2 and $BaSO_4$. (d) Infrared spectrum containing the PVAc binder, $BaSO_4$, $CaCO_3$ and TiO_2.

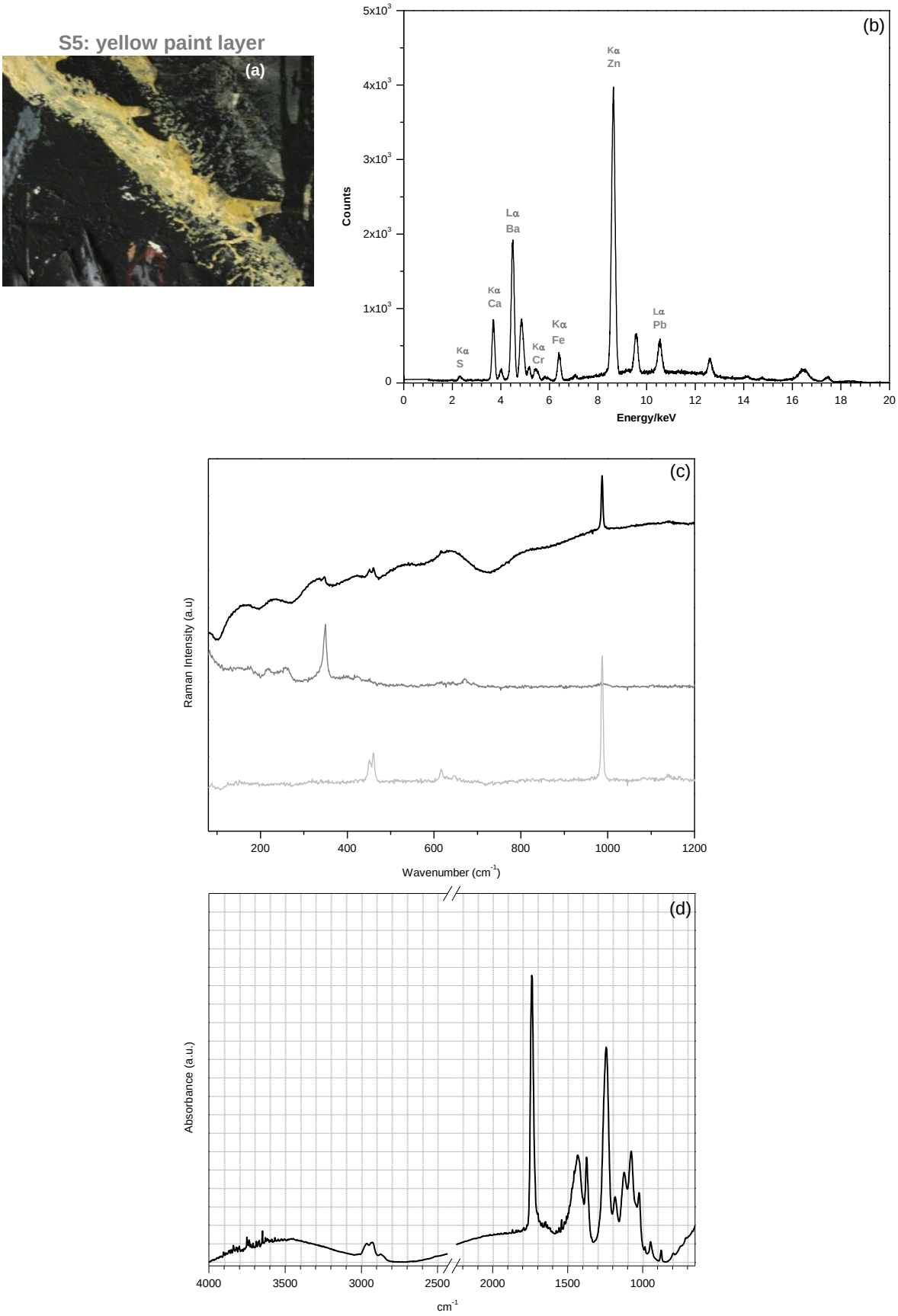


Fig. A5.6: (a) Detail of the paint layer (b) XRF spectrum (c) Raman spectra of the paint sample (—); zinc sulphide (—), barium sulphate (—) (d) Infrared spectrum containing the vinyl binder, $BaSO_4$ and $CaCO_3$.

5.2. *Salto*, 1985-86, (MCB)

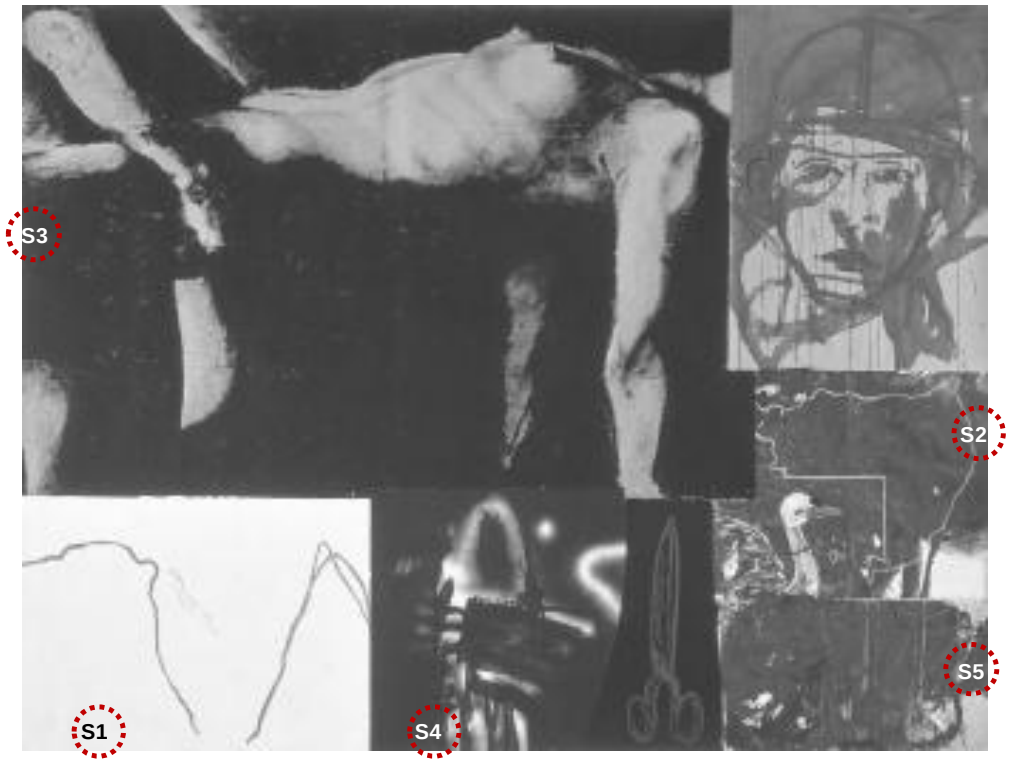


Fig. A5.7: Scheme with the location of the removed samples

Table A5.2: Summary of analytical results of *Salto*

	Colour	Composition
S1	White paint layer	PVAc + VeoVa+ TiO_2 (anatase), $BaSO_4$; $CaCO_3$
S2	Blue paint layer	PVAc as binding medium?; ultramarine blue, carbon black
S3	Black paint layer	PVAc? + magnetite (Fe_3O_4), $CaCO_3$
S4	Bordeaux paint layer	PVA-VeoVa + hematite; carbon black, $CaCO_3$
S5	Brown glue ∗	Polychloroprene

∗ Glue used to adhere the paper to a lining canvas seems to have migrated and contaminated the paint layers.

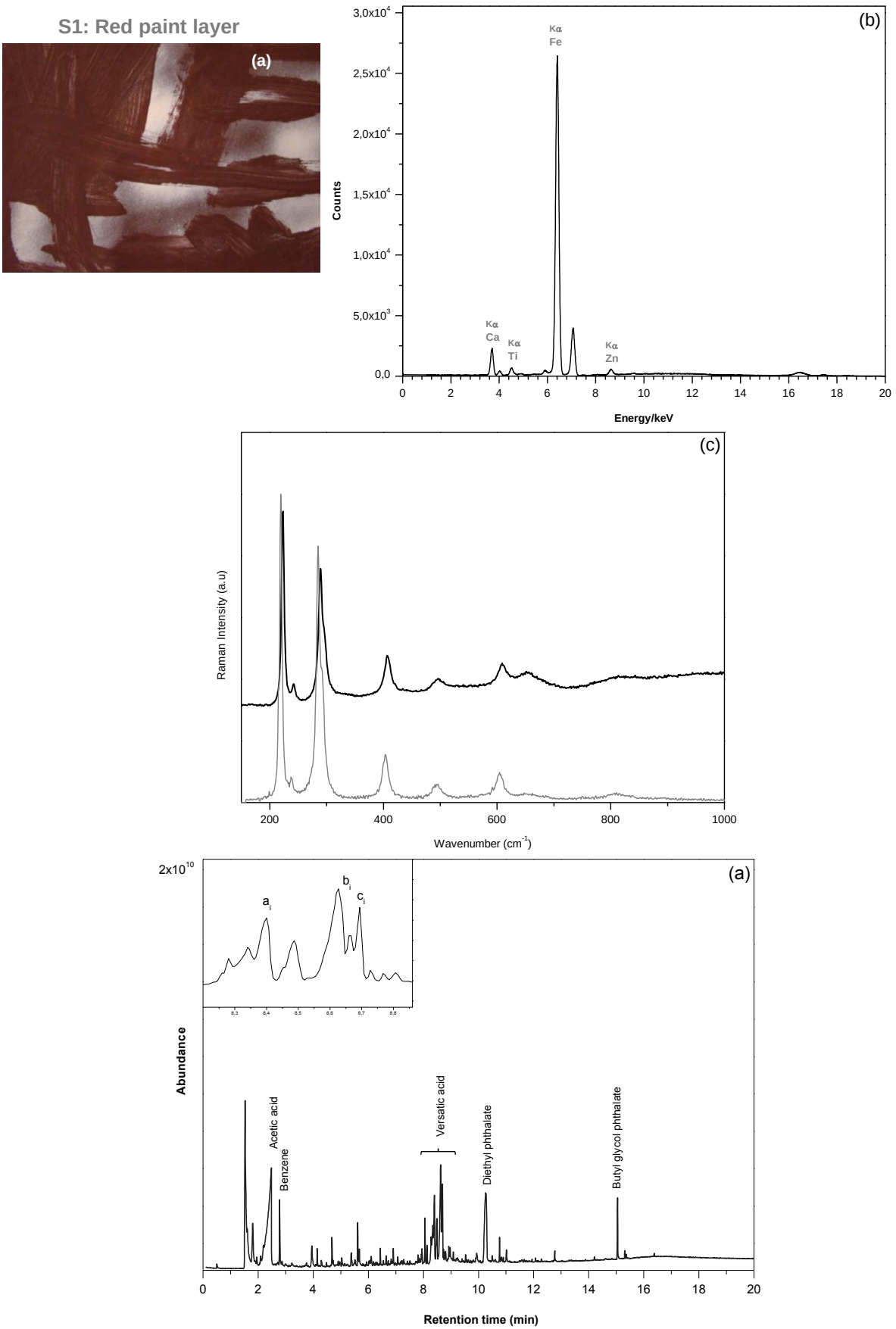


Fig. A5.8: (a) Detail of the red paint layer (b) XRF spectrum (c) Raman spectrum of the red iron oxide (hematite) detected in the paint layer (—) and a reference spectra of hematite (—). (d) Pyrogram showing a PVAc-VeoVa copolymer

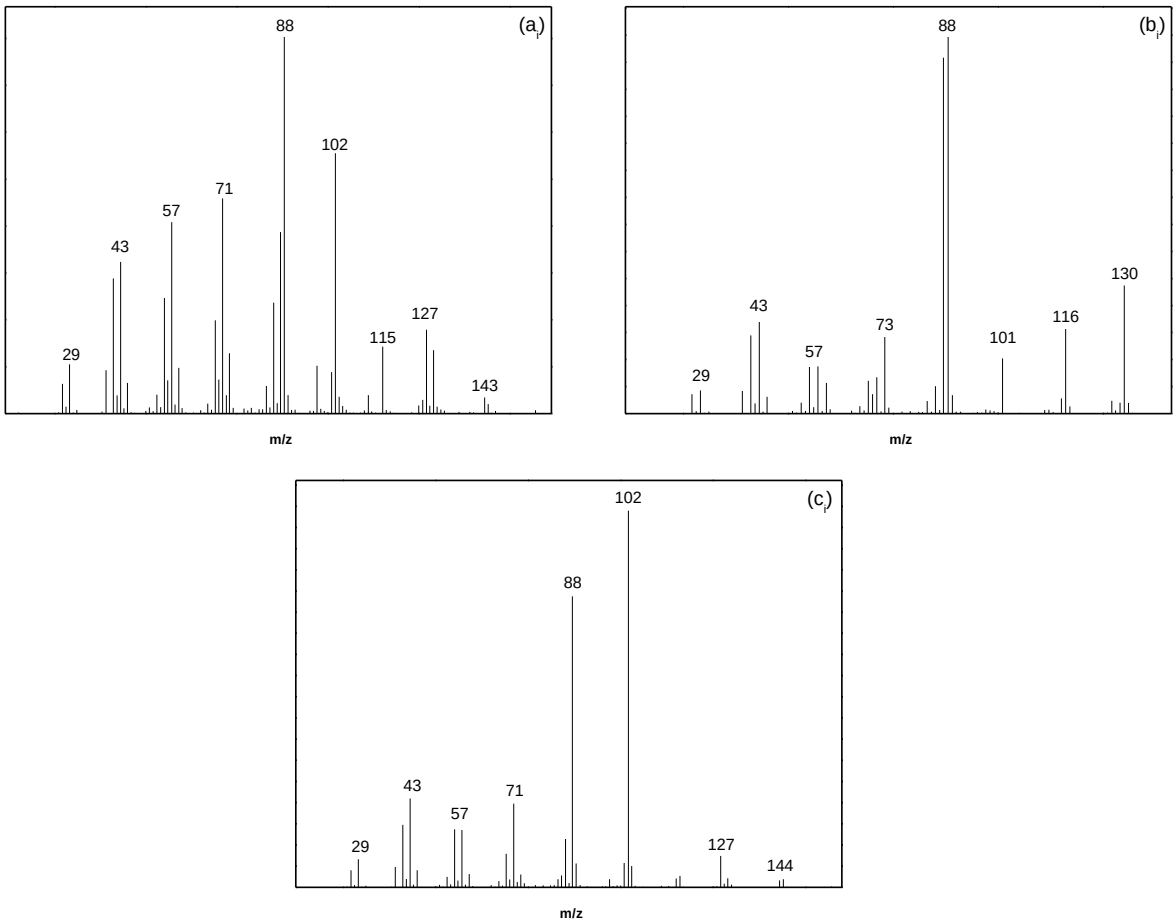


Fig. A5.9: (a_1, b_1, c_1) mass spectra from VeoVa peaks shown in the pyrogram inlay in Fig. A5.8.

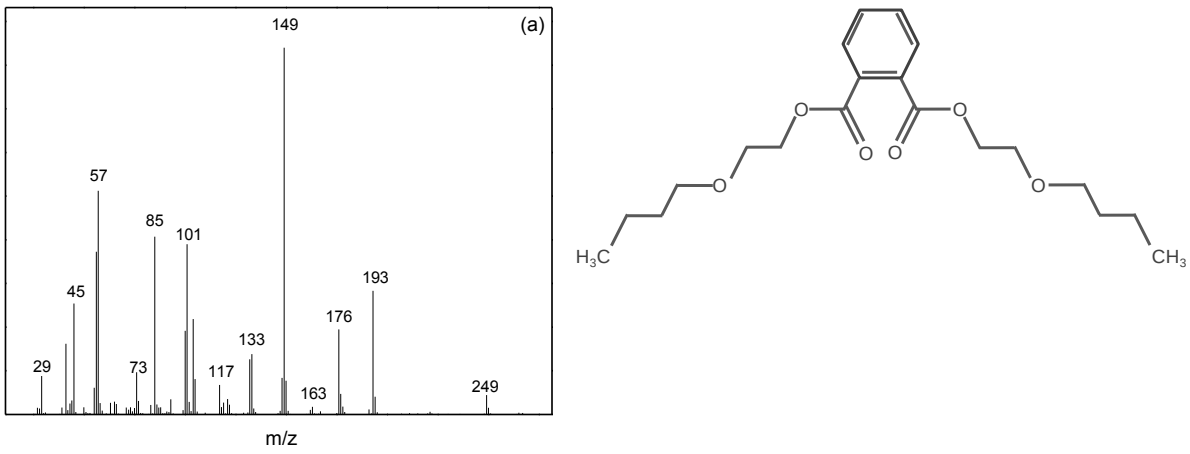
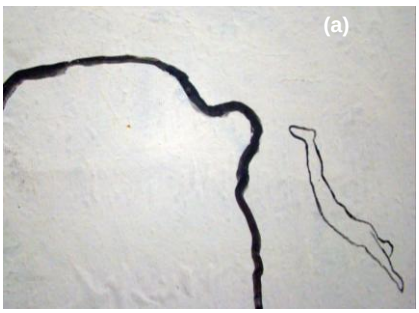
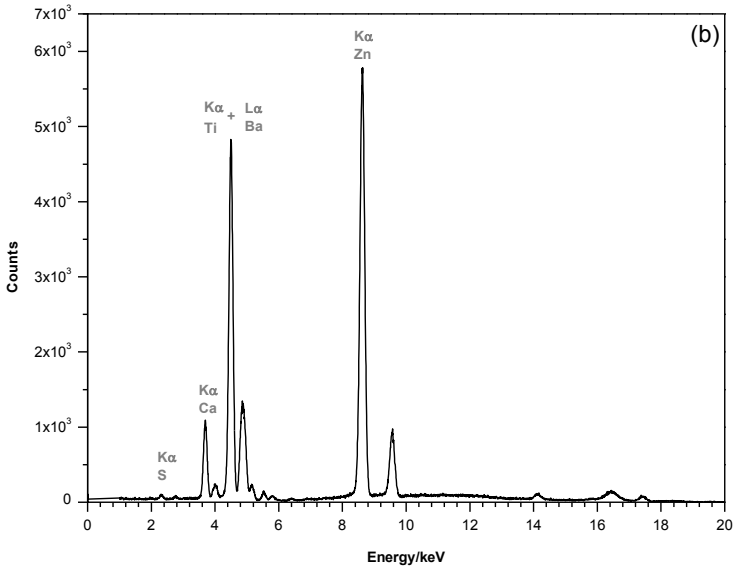
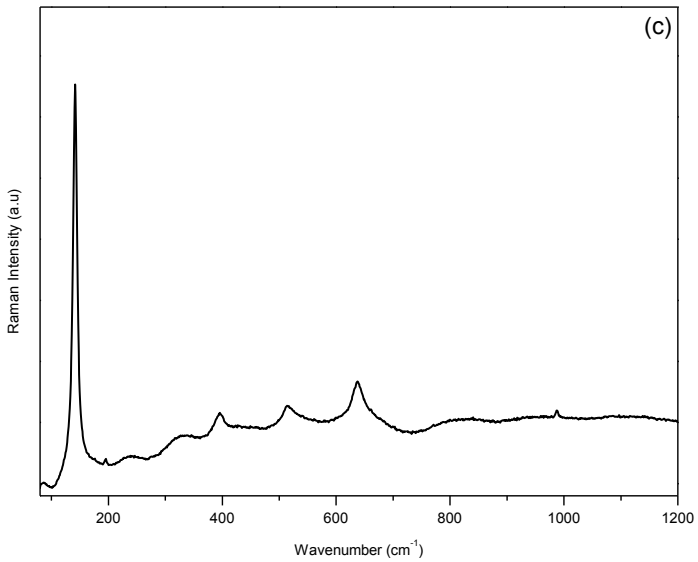


Fig. A5.10: (a) Mass spectrum from DGBE (peak eluting at 15:04min) (b) Diethylene glycol butyl phthalate

S2: White paint layer







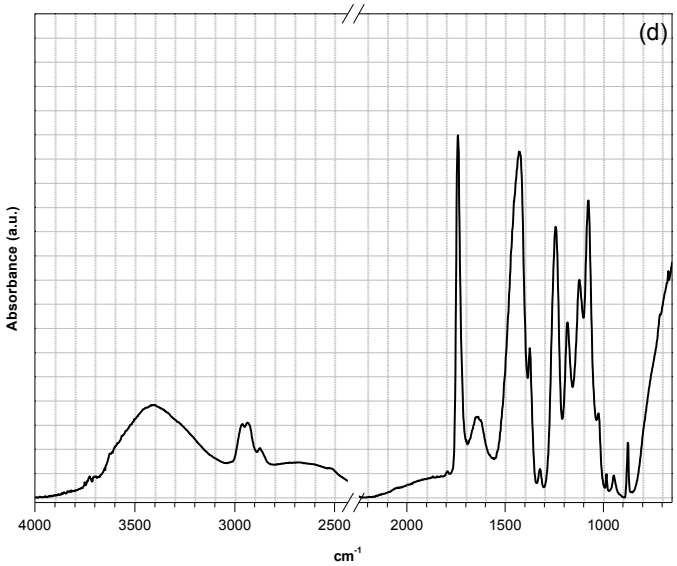


Fig. A5.11: (a) Detail of the white paint layer (b) XRF spectrum (c) Raman spectrum from the white anatase TiO_2 and (d) FTIR spectrum containing the binder $BaSO_4$ and $CaCO_3$.

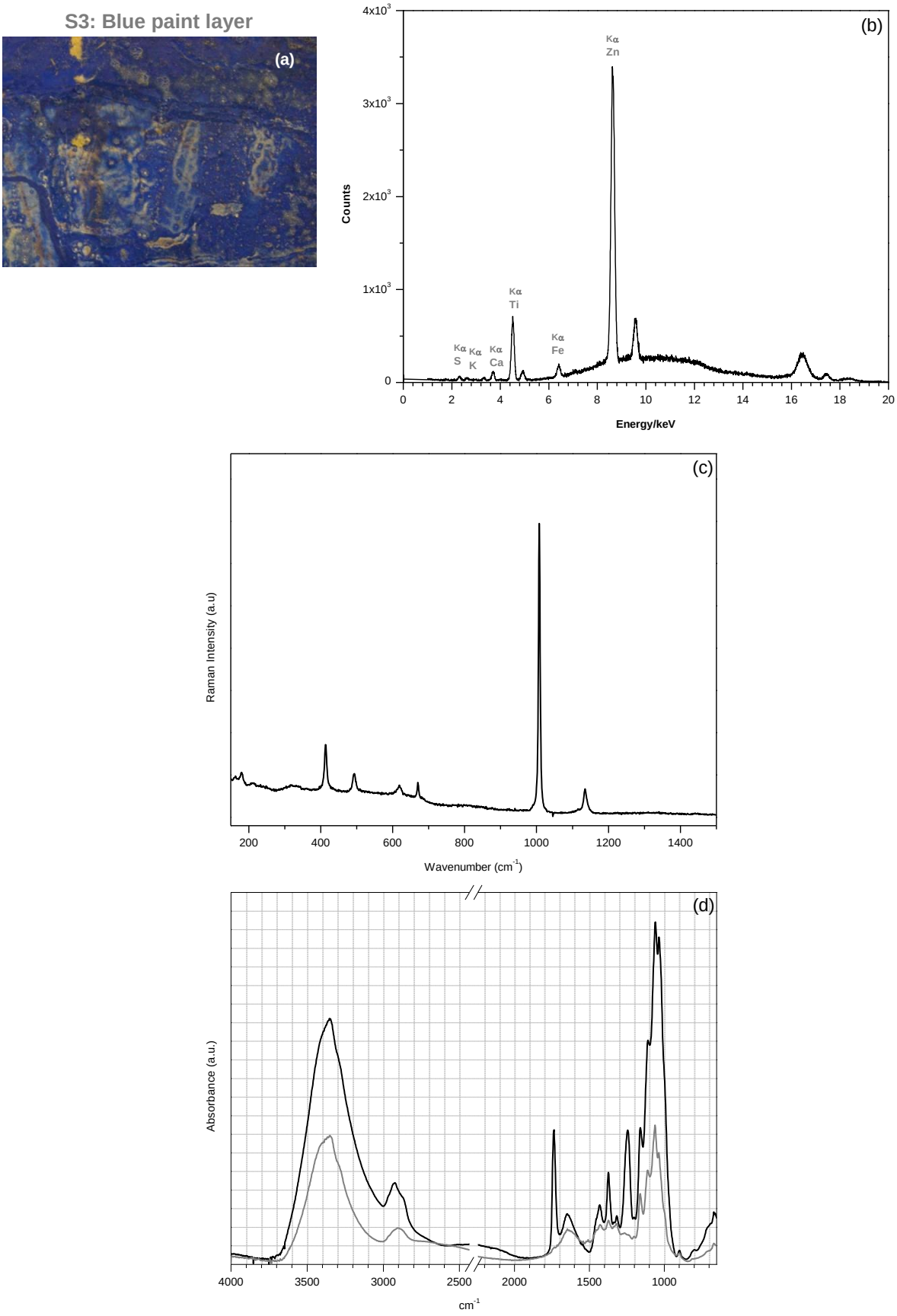


Fig. A5.12: (a) Detail of the blue paint layer (b) XRF spectrum (c) Raman spectrum from the ultramarine blue detected in the paint layer. (d) Infrared spectra showing a PVAc based binder and the impregnation of the paint layers with glue [(—) spectra of the pure brown glue] (see Fig. A5.14)

S4: Black paint layer

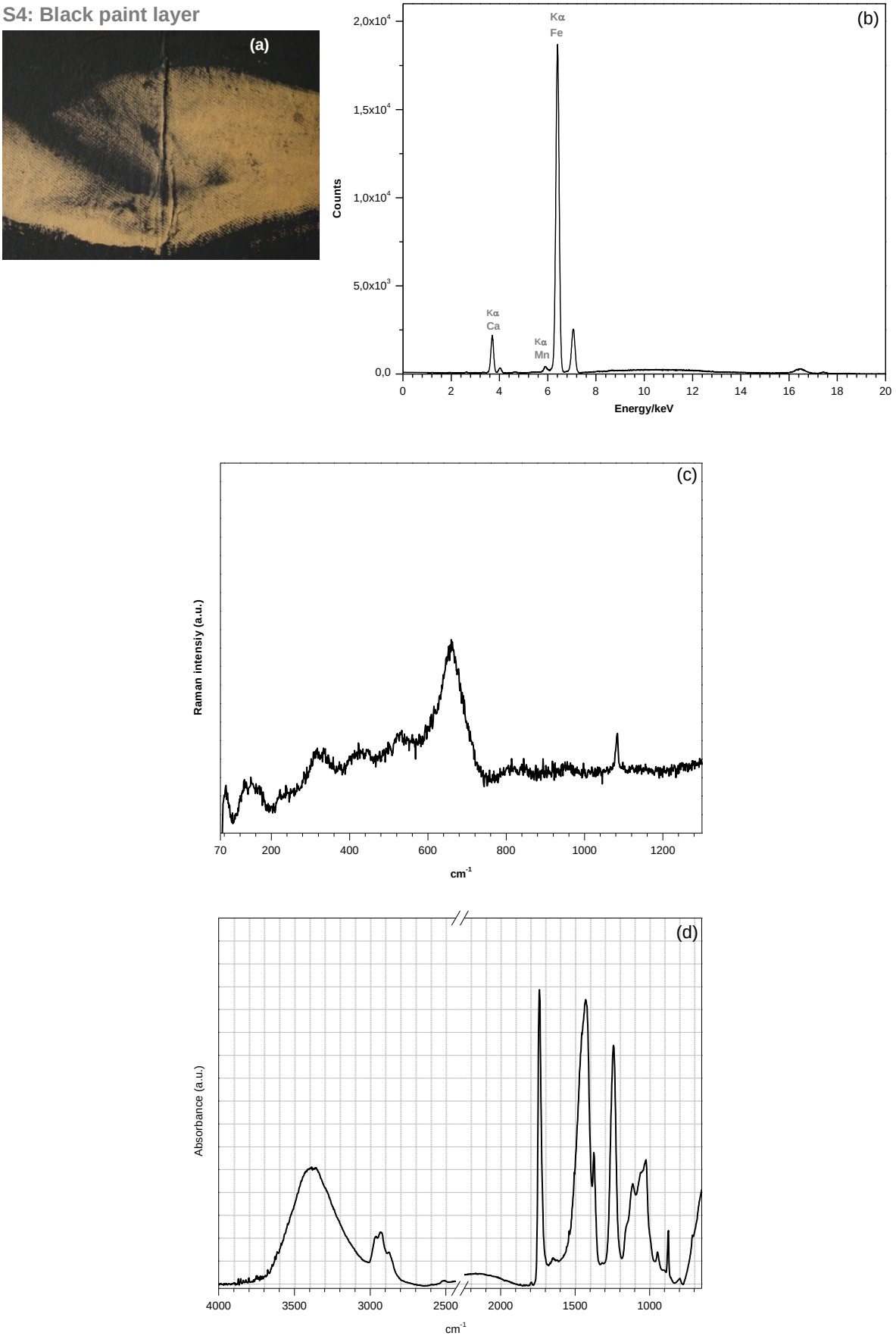


Fig. A5.13: (a) Detail of the black paint layer (b) XRF spectrum (c) Raman spectrum from black iron oxide (magnetite) and some $CaCO_3$. (b) FTIR spectrum showing a PVAc based binder, $CaCO_3$ and from the glue contaminating the sample (see Fig. A5.14).

S5: Glue used for lining

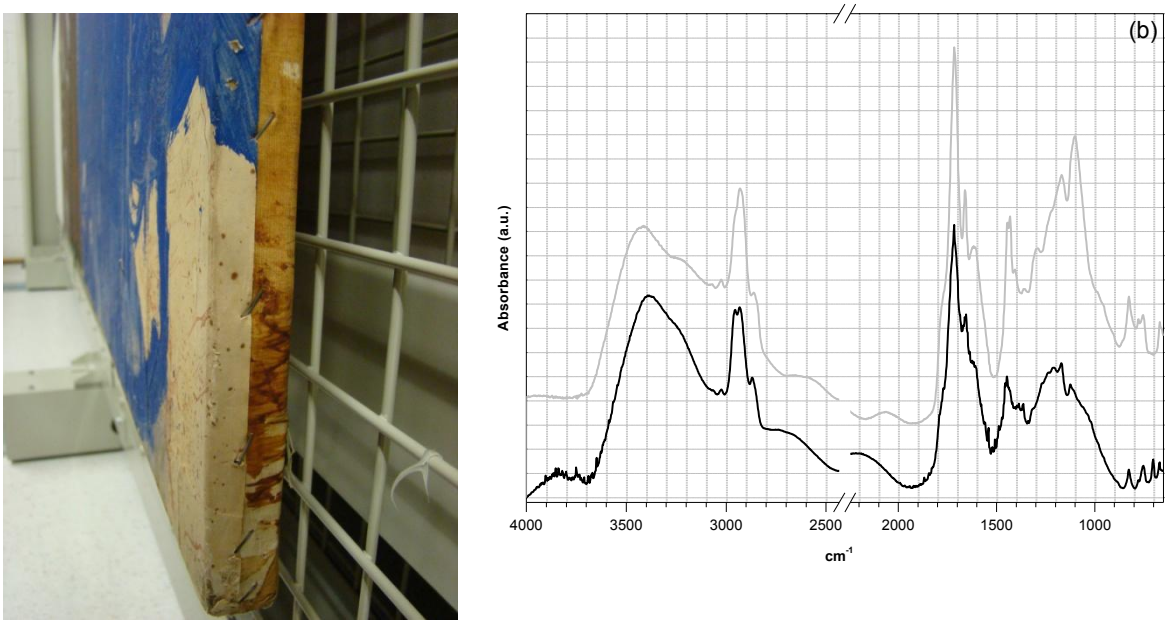


Fig. A5.14: (a) Detail of the brown glue used to attach the paper to a textile support. (b) FTIR spectrum from the brownish adhesive a chloroprene based glue (—) and spectrum from a degraded similar glue used as a reference spectrum. [150]

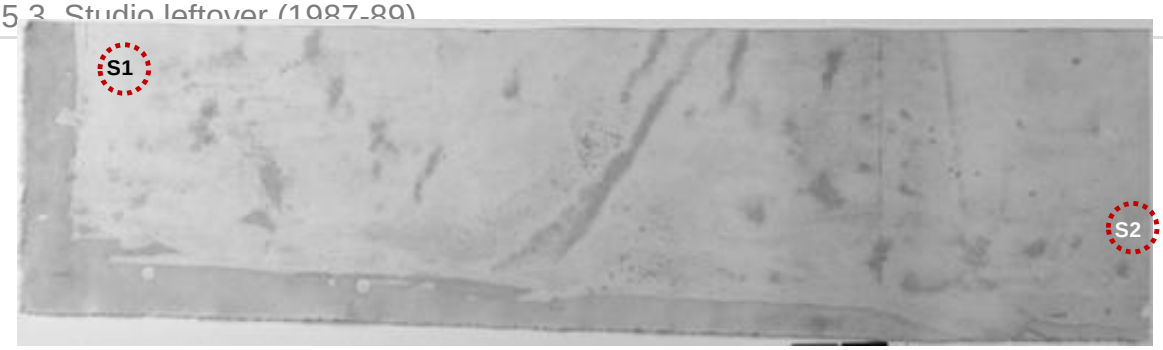


Fig. A5.15: Scheme with the location of the removed samples

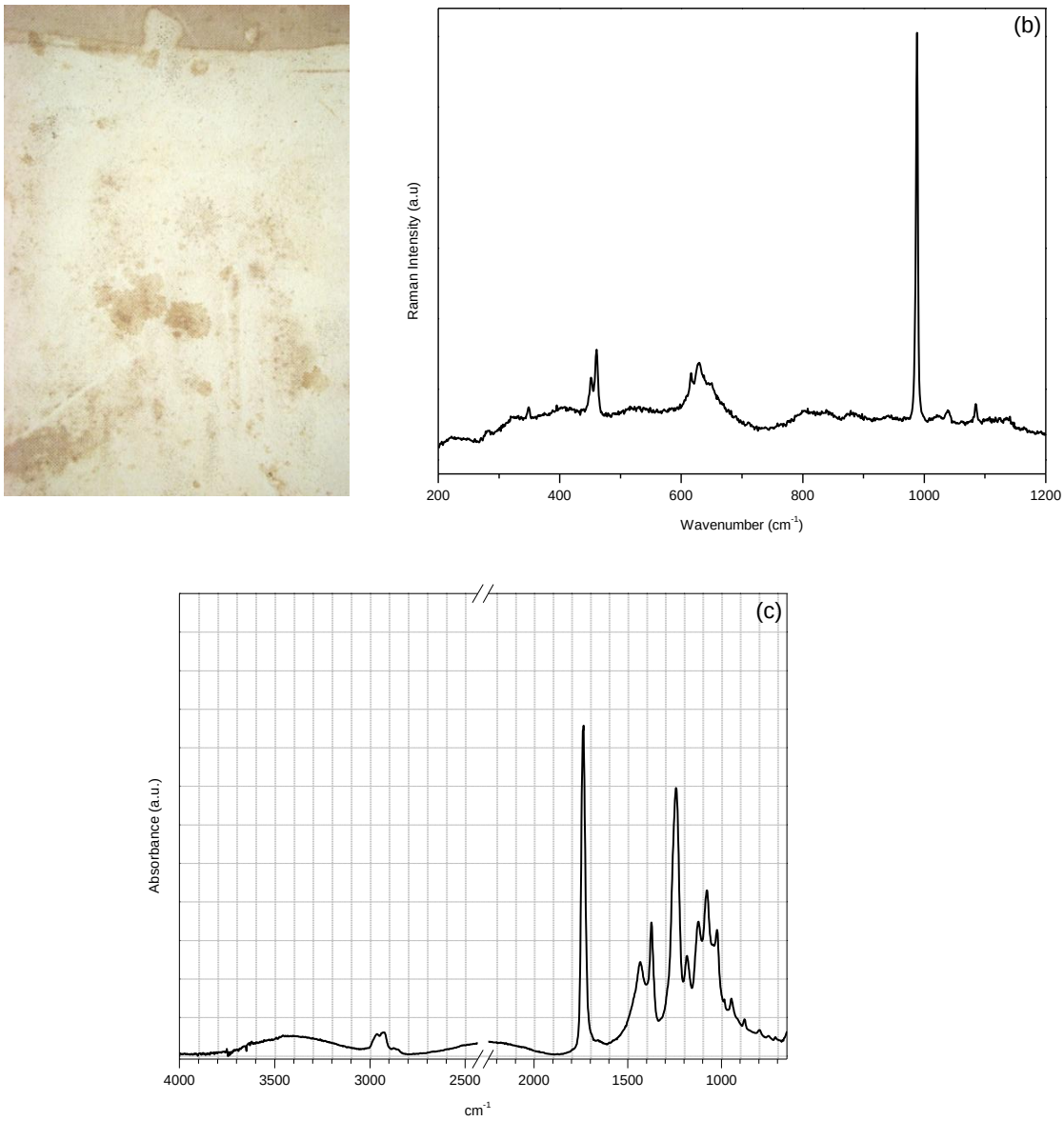


Fig.A5.16: (a) Detail of the paint layer (b) Raman spectrum from lithopone white pigment. (c) FTIR spectrum showing a PVAc based binder, $BaSO_4$ and $CaCO_3$.

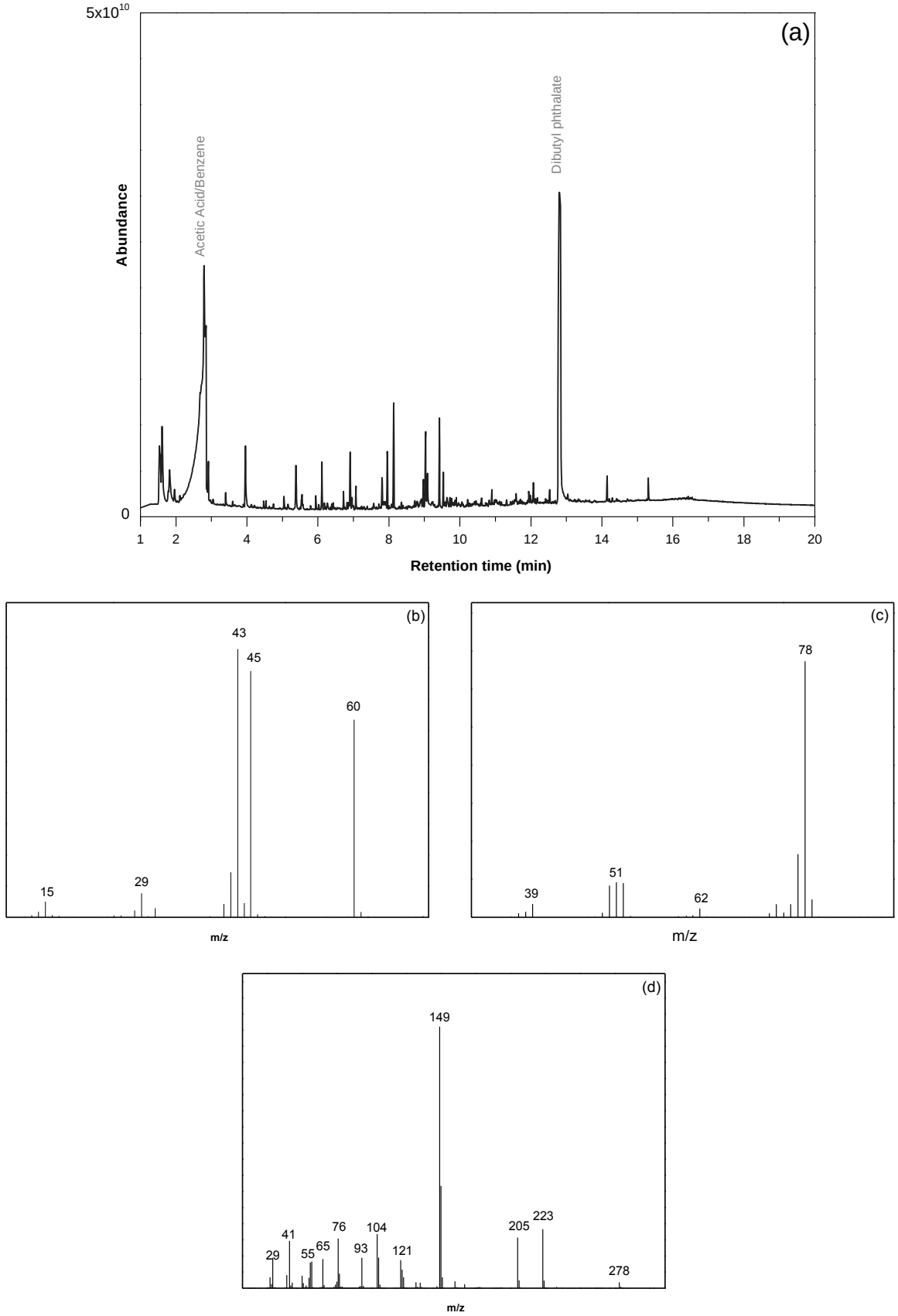


Fig. A5.17: (a) White paint pyrogram showing a PVAc homopolymer; (b) mass spectrum of acetic acid (peak eluting at 2:73min) (c) mass spectrum from benzene (peak eluting at 2:78min) (d) mass spectrum dibutyl phthalate (peak eluting at 12:80min).

Table A5. 3: Molecular species produced on the pyrolysis of a sample from the studio leftover from the 90's, the corresponding retention time, molecular weight and m/z values

Molecular species	Retention time	Mw	m/z values
Carbon dioxide	1:53	44	44
Acetone	1:81	58	43,58
1,3 - cyclopentadiene	1:95	66	66,39
Acetic Acid	2:73	60	60,43
Benzene	2:78	78	78,51
1-Butanol	2:84	74	56,41,31
Acetic anhydride	3:39	102	43,15
Toluene	3:95	92	91,65
Ethylbenzene	5:04	106	91,106
styrene	5:38	104	104,78,51
cyclopropylbenzene	5:94	118	117,91
propylbenzene	6:02	120	91,12
benzaldehyde	6:11	106	106,77,51
1-propenyl-benzene	6:72	118	117,91
Indane	6:82	118	117
3 - butenyl-benzene	6:86	132	91,132
1H-Indene	6:91	116	116
phenyl ester acetic acid	6:96	136	94,43,136,39,66
Acetophenone	7:07	120	105,77,120,51
1,4 - dihydronaphthalene	7:81	130	130,115
1,2 - dihydronaphthalene	7:95	130	130,115,64
naphthalene	8:13	128	128
2-methyl-naphthalene	8:97	142	142,115
phthalic anhydride	9:02	148	104,76,50,148
1-methyl-naphthalene	9:09	142	142,115
Butyl benzoate	9:42	178	105,123,77,56
biphenyl	9:53	154	154,76,51
Diisobutyl phthalate	12:28	149	149,223, 57, 104
Dibutyl phthalate	12:80	278	149,205,57,104
butyl-2-ethylhexyl ester phthalic acid	14:40	334	149,223
…phthalate	15:05	366	149,57,85,101,193,176,133
Diisoctyl phthalate	15:31	390	149,167,57,71,279

5.4. *Pintura Cega (Quatro Instrumentos de prazer e um de dor)*, 1990

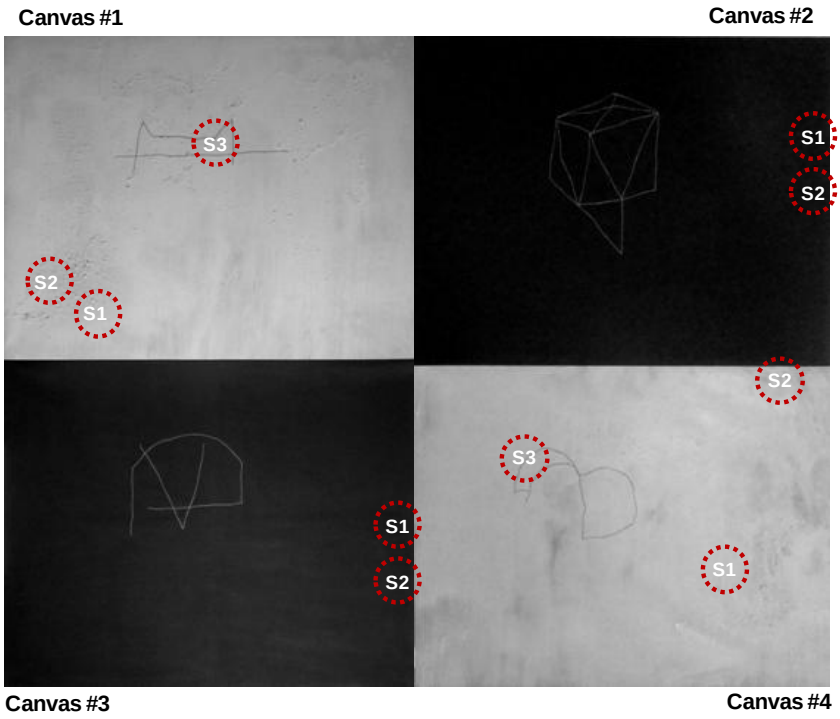
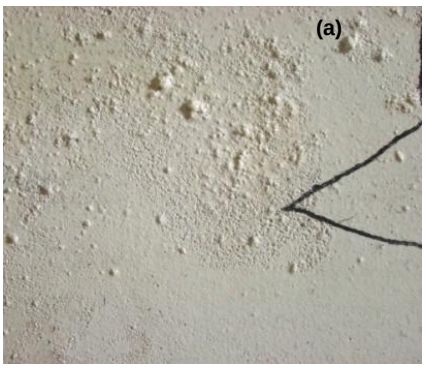


Fig. A5.18: Scheme with the location of the removed samples

Table A5.4: Summary of analytical results of *Pintura Cega (Quatro instrumentos de prazer e um de dor)*

	Colour	Composition
	Canvas # 1	
S1	Dry pigment	Lithopone, Calcium carbonate
S2	White paint layer	PVAc + Lithopone, Calcium carbonate
S2	Black drawing	Charcoal (?)
	Canvas # 2	
S1	Top black paint layer	PVAc + Carbon Black
S2	Underlying black paint layer	PVAc + Carbon Black
	Canvas # 3	
S1	Top black paint	PVAc + Carbon Black + $CaCO_3$
S2	Underlying black paint layer	PVAc + Carbon Black
	Canvas #4	
S1	Dry pigment	Lithopone, Calcium carbonate
S2	White paint layer	PVAc + Lithopone, Calcium carbonate
S3	Black drawing	Carbon black (?)

Canvas #1: S1 and S2:
White paint layer and black drawing



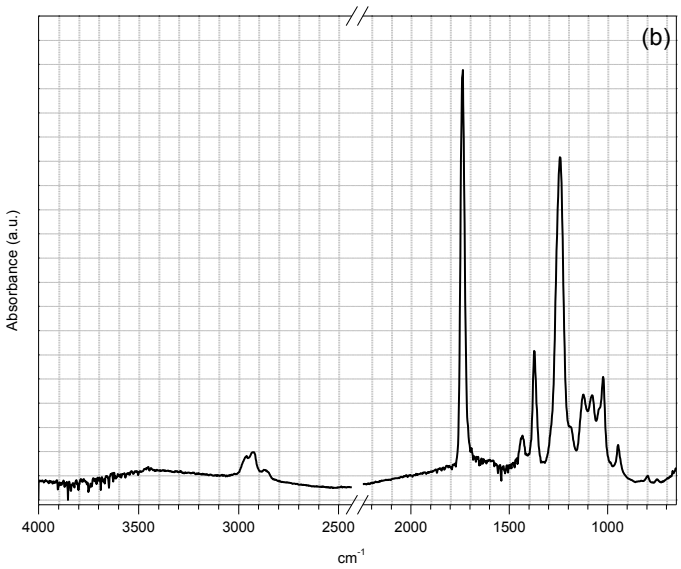
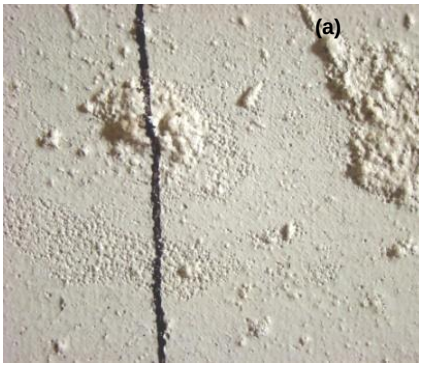
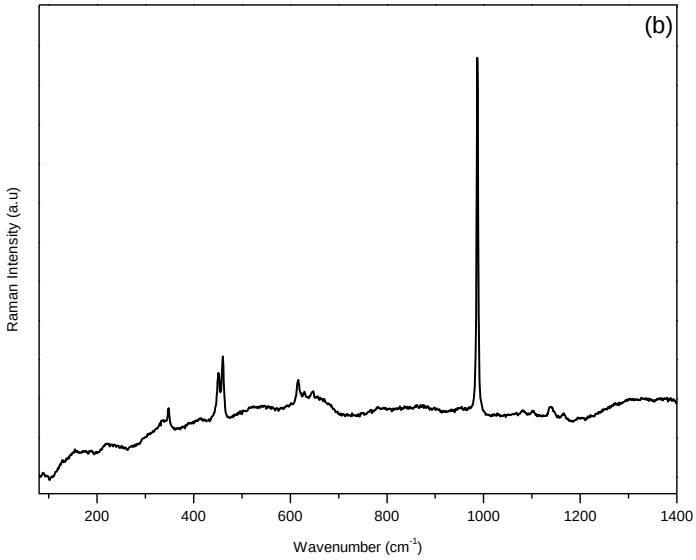
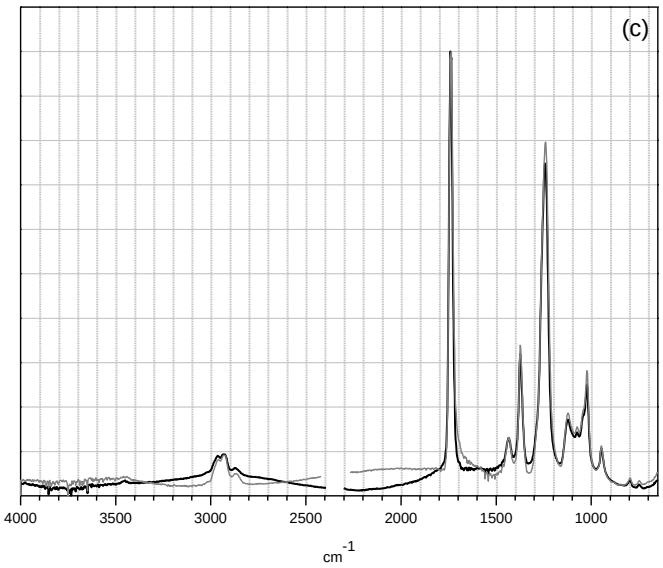


Fig.A5.19: (a) Detail of canvas #1 (b) FTIR spectrum of the PVAc binding medium in the white layer (c) Raman spectra of carbon black (charcoal?) in the drawing.

Canvas #1: S1 and S2:
White paint layer and black drawing







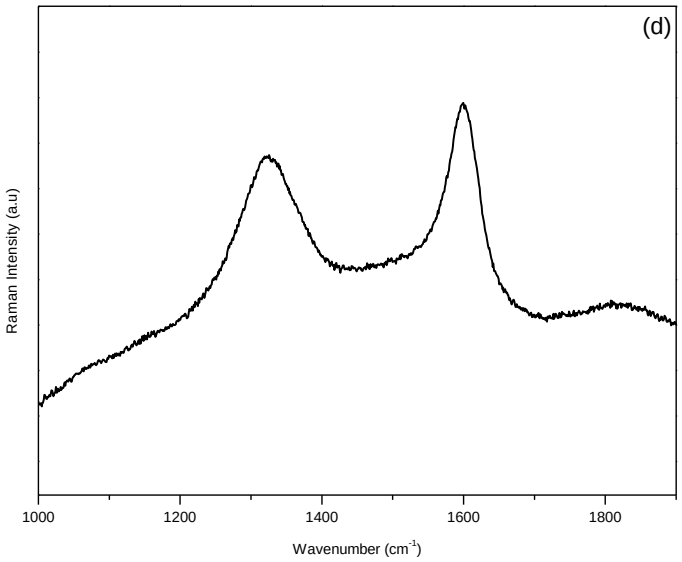


Fig.A5.20: (a) Detail of Canvas #4 (b) Raman spectra of the dry pigment lithopone. (c) FTIR spectra of the PVAc binding medium from a white area (—) and from a discolored area (—). (d) Raman spectra of carbon black from the black drawing.

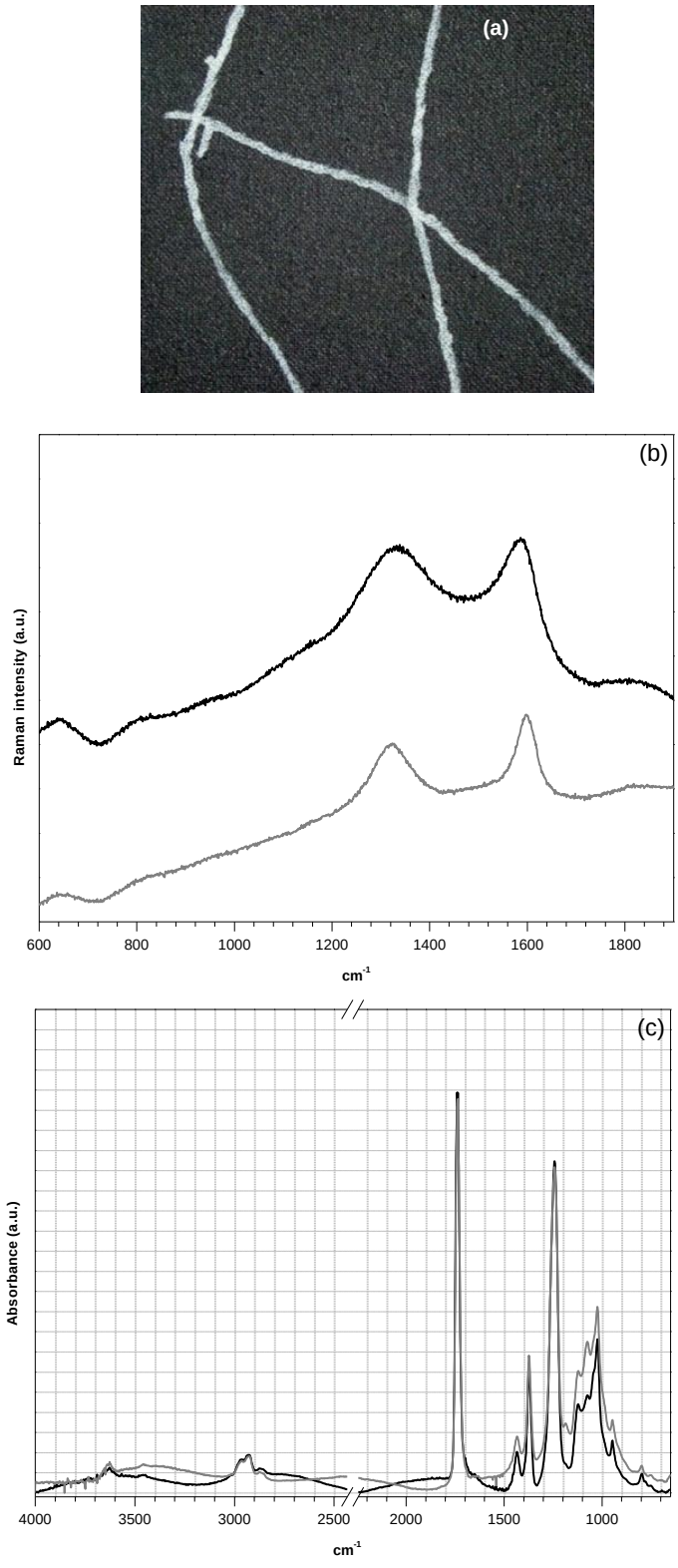


Fig.A5.21: (a) detail of Canvas #2 (b) Raman spectrum of carbon black (—) top paint layer (—) underlying paint layer. (c) FTIR spectrum of the PVAc binding medium (—) top paint layer (—) underlying paint layer.

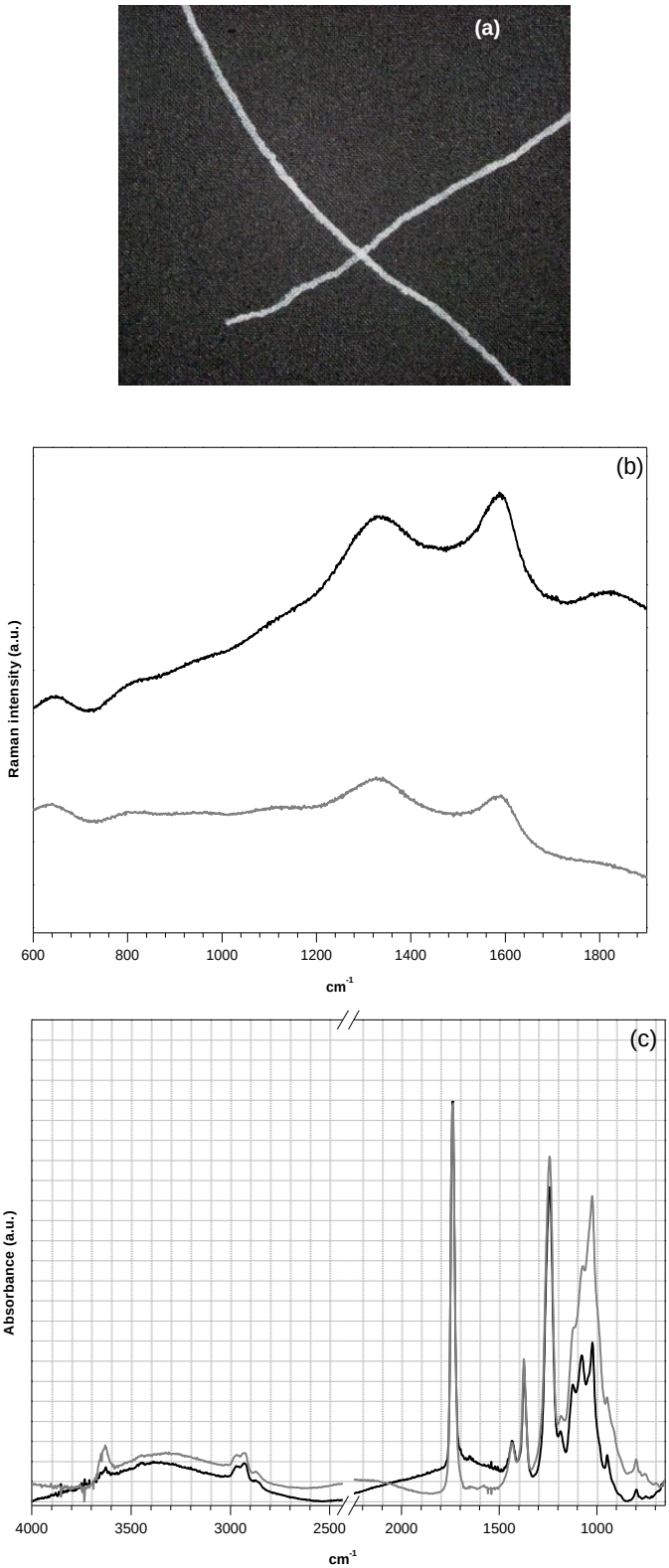


Fig.A5.22: (a) detail of Canvas #3 (b) Raman spectra of carbon black (—) top paint layer (—) underlying paint layer. (c) FTIR spectra of the PVAc binding medium (—) top paint layer (—) underlying paint layer.

5.5. *I don't want to go to sleep*, 1991 (Culturgest)

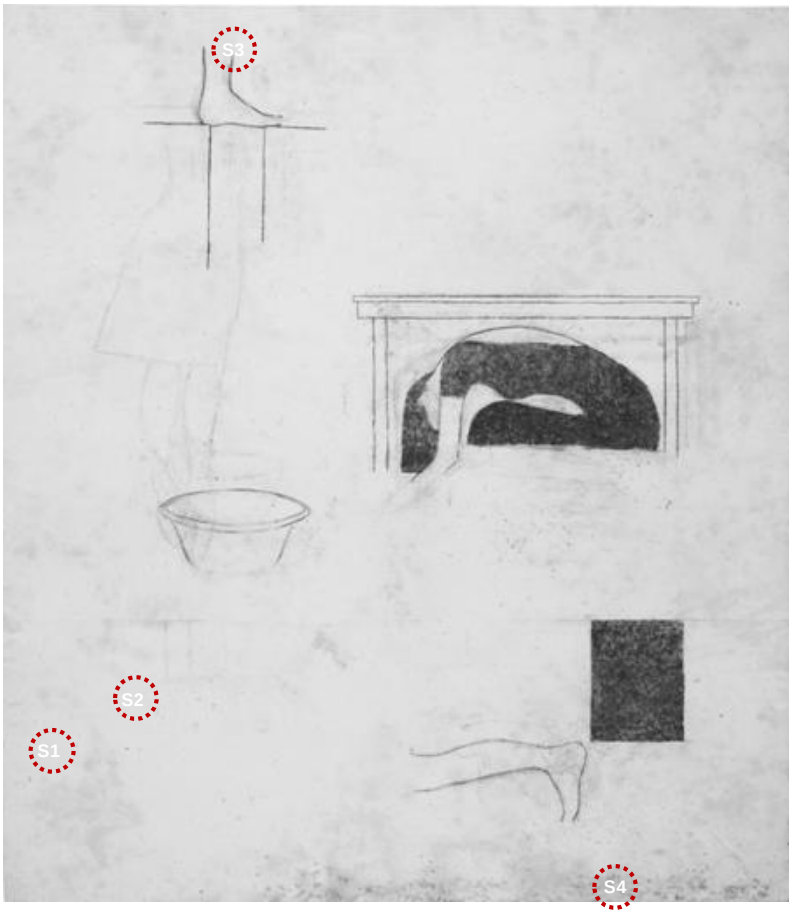
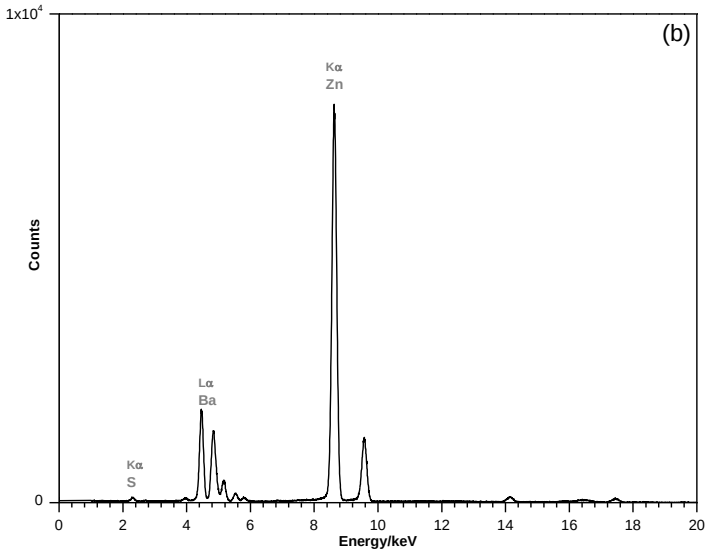


Fig. A5.23: Scheme with the location of the removed samples

Table A5.5: Summary of analytical results of *I don´t want to go to sleep*

	Colour	Composition
S1	Dry white pigment	Lithopone
S2	White paint layer	PVAc + Lithopone + $CaCO_3$
S3	Grey area	PVAc
S4	Black drawing	Graphite

S1 and S2: Dry white pigment and white paint layer



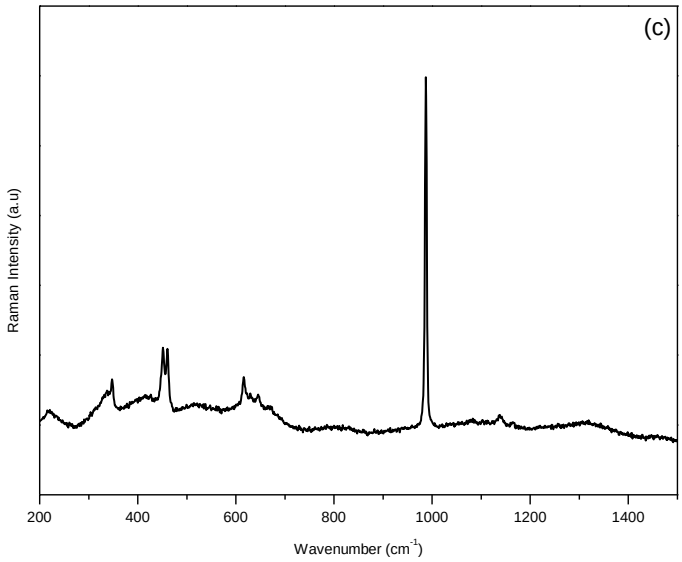


Fig.A5.24: (a) Detail of the white paint layer. (b) XRF spectra. (c) Raman spectra of dry pigment lithopone.

S3: Greyish layer

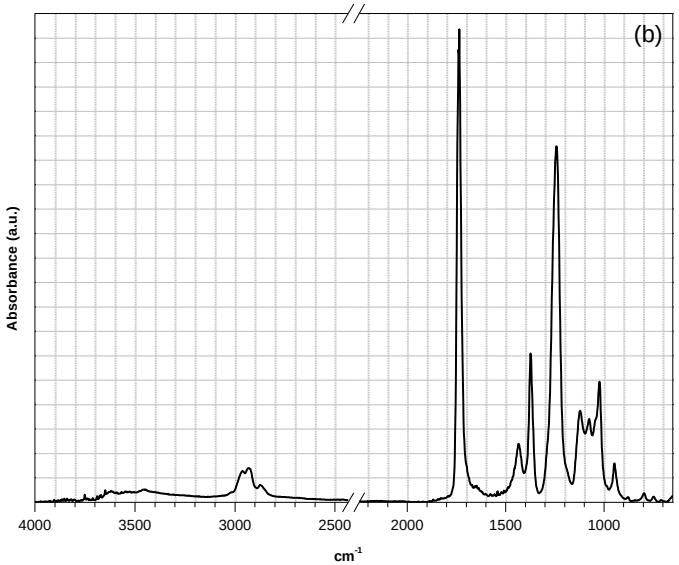
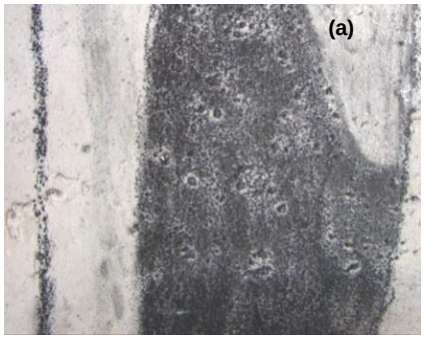


Fig.A5.25: (a) Detail of grey area (supposedly through contact with water). (b) FTIR spectra

S4: Black drawing



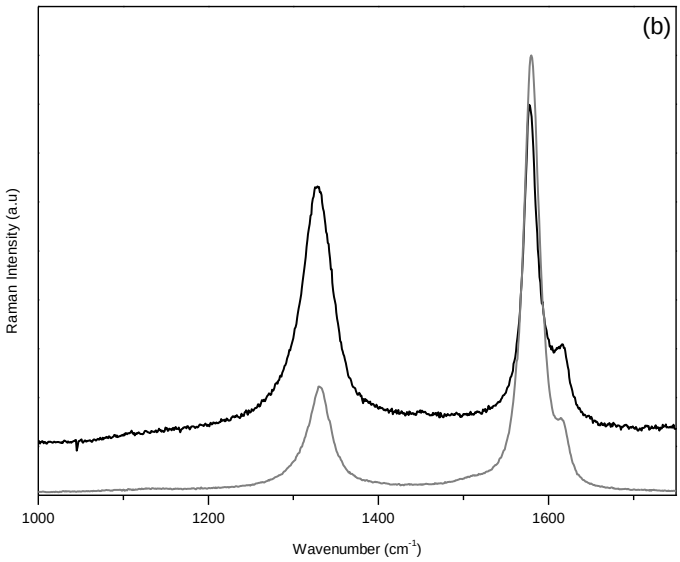


Fig.A5.26: (a) Detail of the drawing (b) Raman spectrum of graphite from the black drawing (—) and reference spectra of graphite (—).

5.6. *Wasting my time with you*, 1991 (MCB)

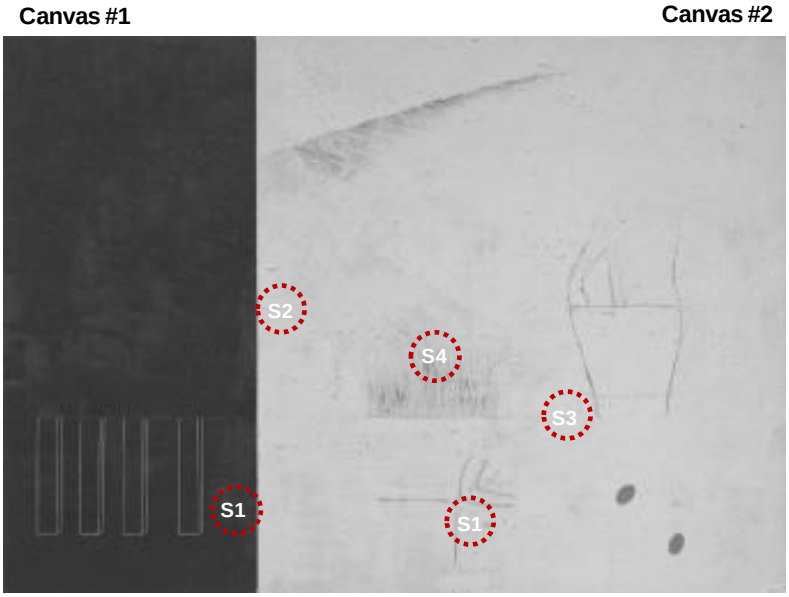


Fig.A5.27: Scheme with the location of the removed samples

Table A5.6: Summary of analytical results of *Wasting my time with you*

	Colour	Composition
	Canvas # 1	
S1	Black paint layer	PVAc + carbon black, $CaCO_3$
	Canvas # 2	
S1	Dry pigment	Lithopone
S2	White paint layer	PVAc + Lithopone, $CaCO_3$
S3	Yellowed binding medium	PVAc
S4	Black drawing	Graphite

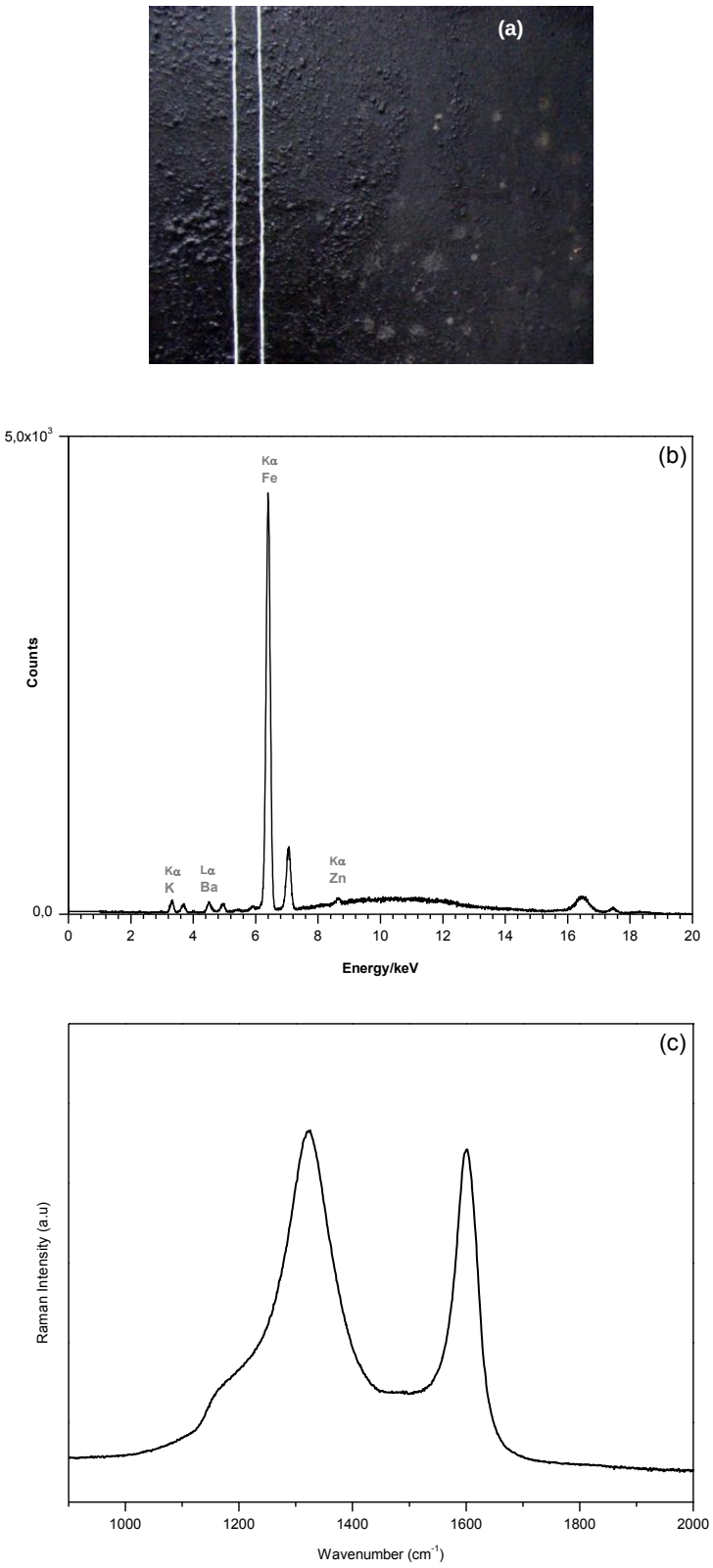


Fig.A5.28: (a) Detail of the black in canvas #1. (b) XRF spectrum (c) Raman spectrum of carbon black in the paint layer.

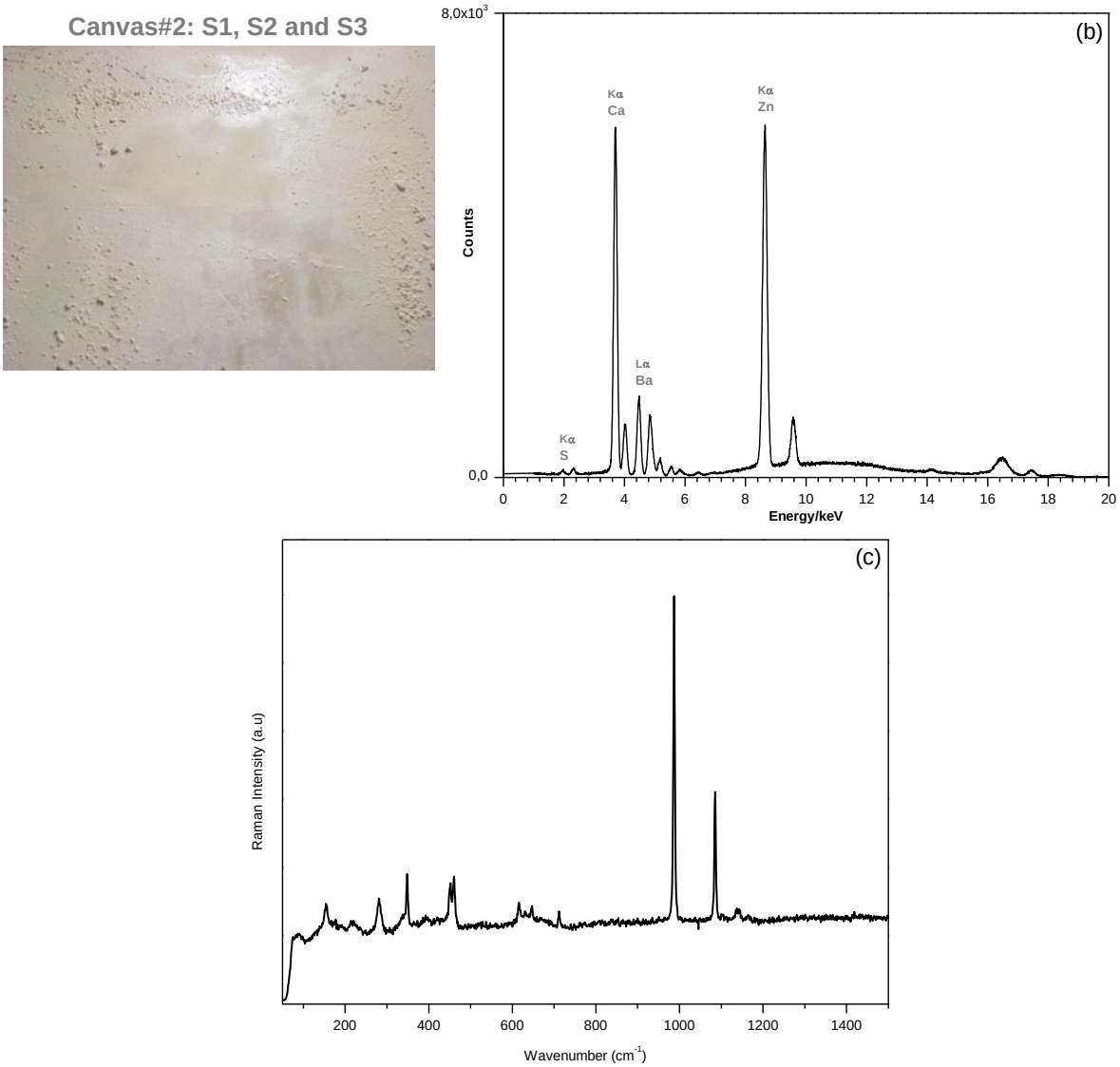


Fig.A5.29: (a) Detail of the white paint layer. (b) XRF spectrum (c) Raman spectrum of the pigment lithopone.

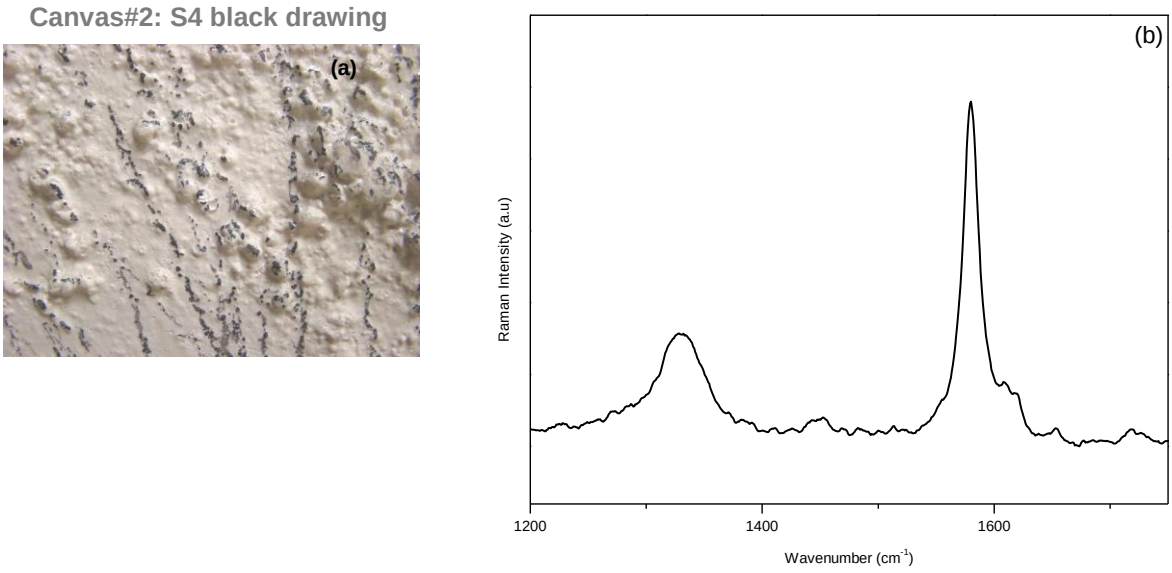


Fig.A5.30: (a) Detail of the drawing in *I don´t want to go to sleep*. (b) Raman spectrum of graphite from the drawing.

5.7. *Frozen Leopard*, 1991-92 (FCG-CAM)

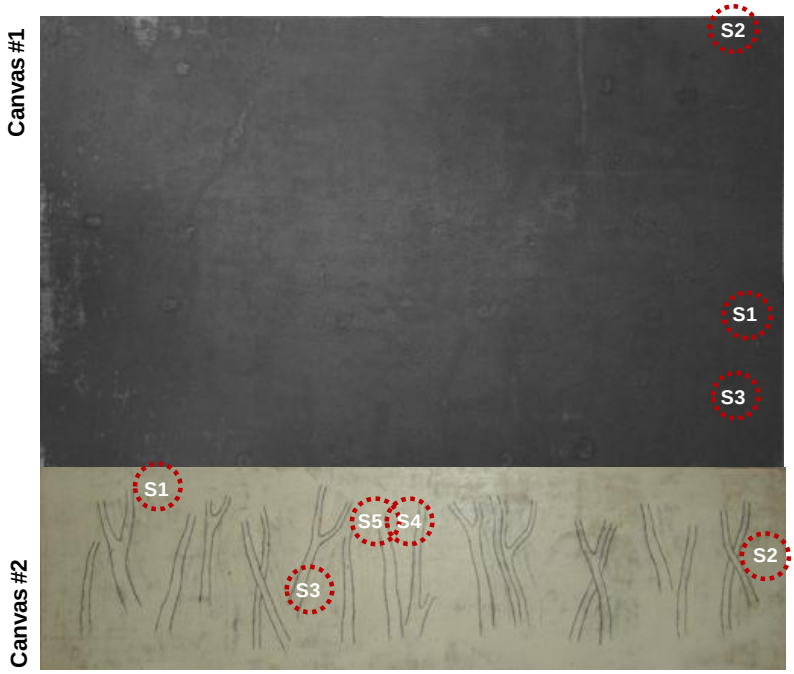


Fig. A5.31: Scheme with the location of the removed samples

Table A5.7: Summary of analytical results of *Frozen Leopard*

	Colour	Composition
	Canvas # 1	
S1	Red paint layer	PVAc
S2	Drawing	Graphite
S3	Red dry pigment	Fe_2O_3
	Canvas # 2	
S1	White paint layer	PVAc + Lithopone, $CaCO_3$
S2	Dry pigment	Lithopone
S3	Black drawing	Graphite
S4	Black drawing + fixative	PVAc + Acrylic
S5	Yellowed binding medium	PVAc

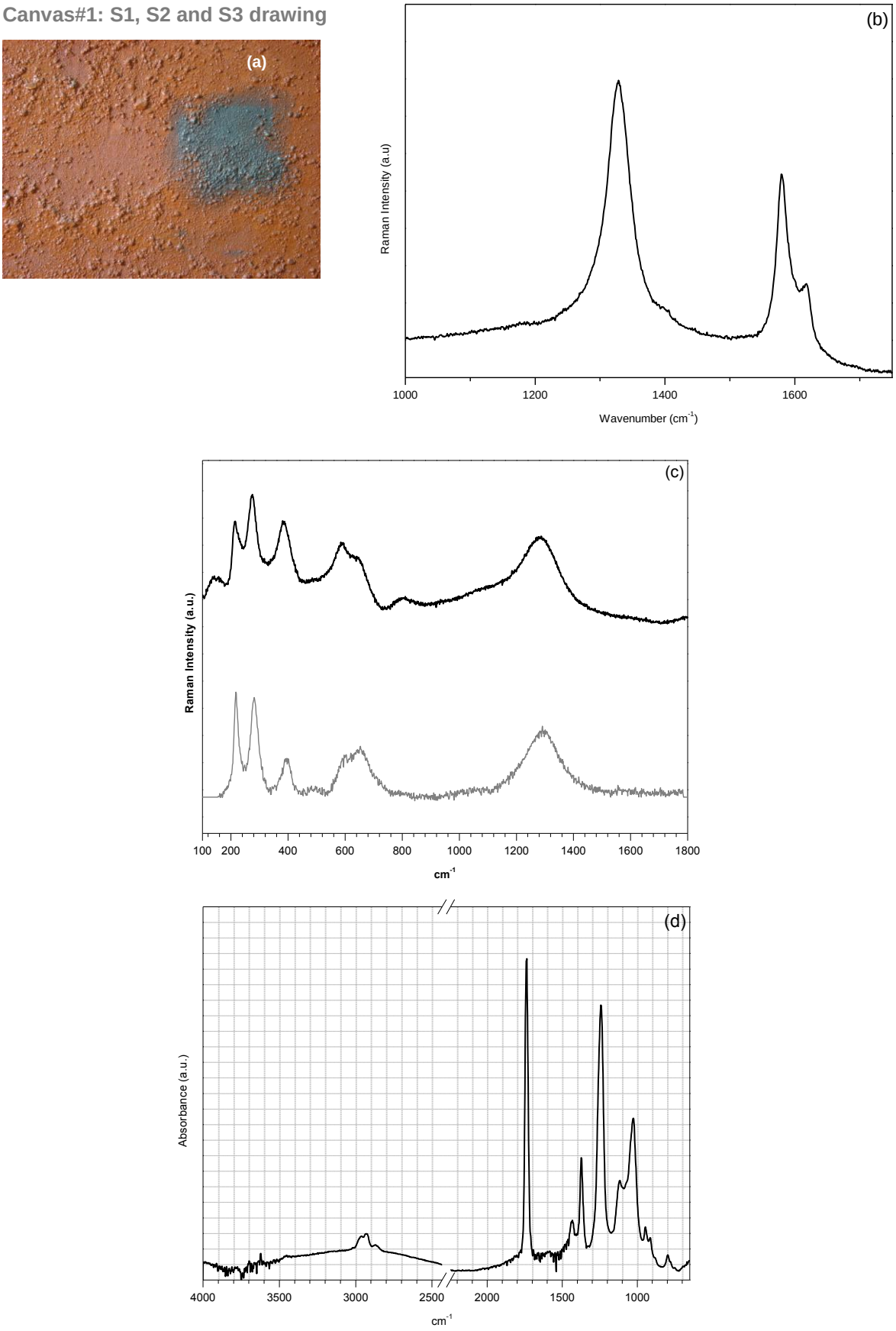


Fig.A5.32: (a) Detail of the red paint layer and black drawing in canvas #1. (b) Raman spectrum of graphite. (c) Raman spectra of the red pigment (—) and reference spectra of Burnt umber (Fe_2O_3 + MnO) (—). (d) FTIR spectrum of the PVAc binding medium.

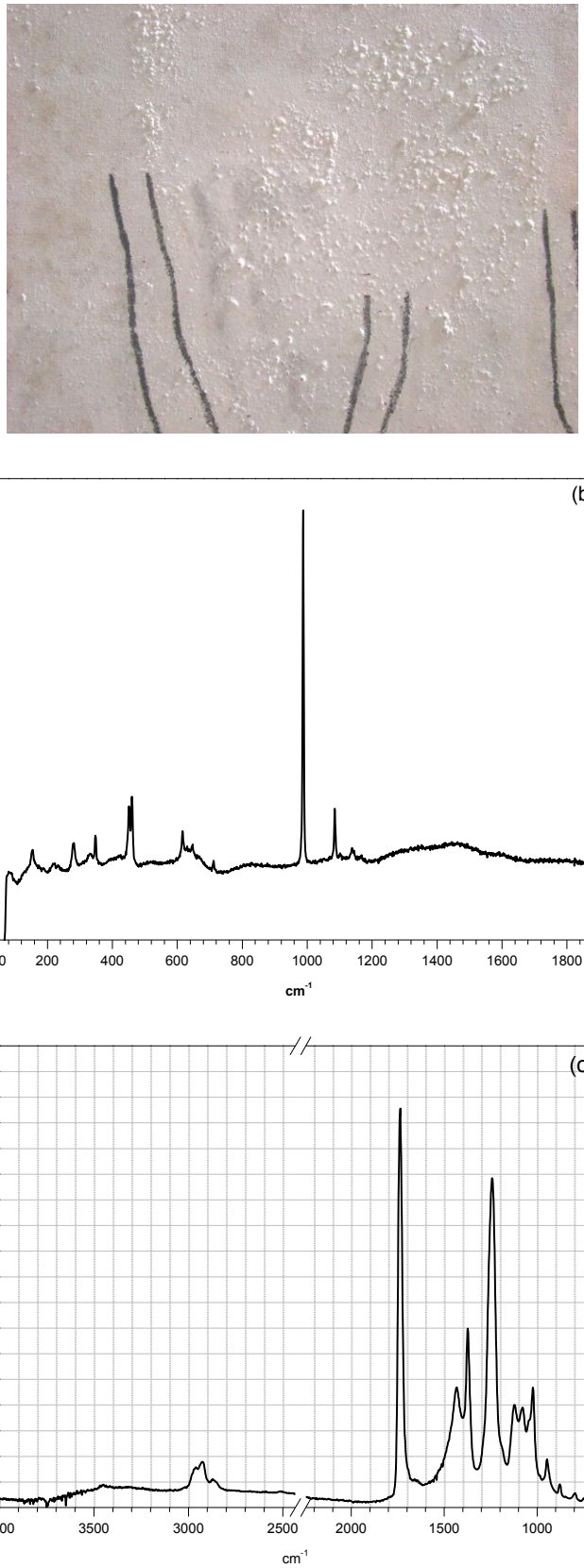


Fig.A5.33: (a) Detail of the white paint layer in canvas #2. (b) Raman spectrum of lithopone and $CaCO_3$. (d) FTIR spectrum of the PVAc binding medium and $BaSO_4$.

5.8. Belém, 1992 (Centro Cultural de Belém)

Fig. A5.34: Scheme with the location of the removed samples

Table A5.8: Summary of analytical results of *Belém*

	Colour	Composition
S1	Dry pigment	Lithopone
S2	White paint layer	PVAc + Litophone+$CaCO_3$
S3	Black drawing	Graphite

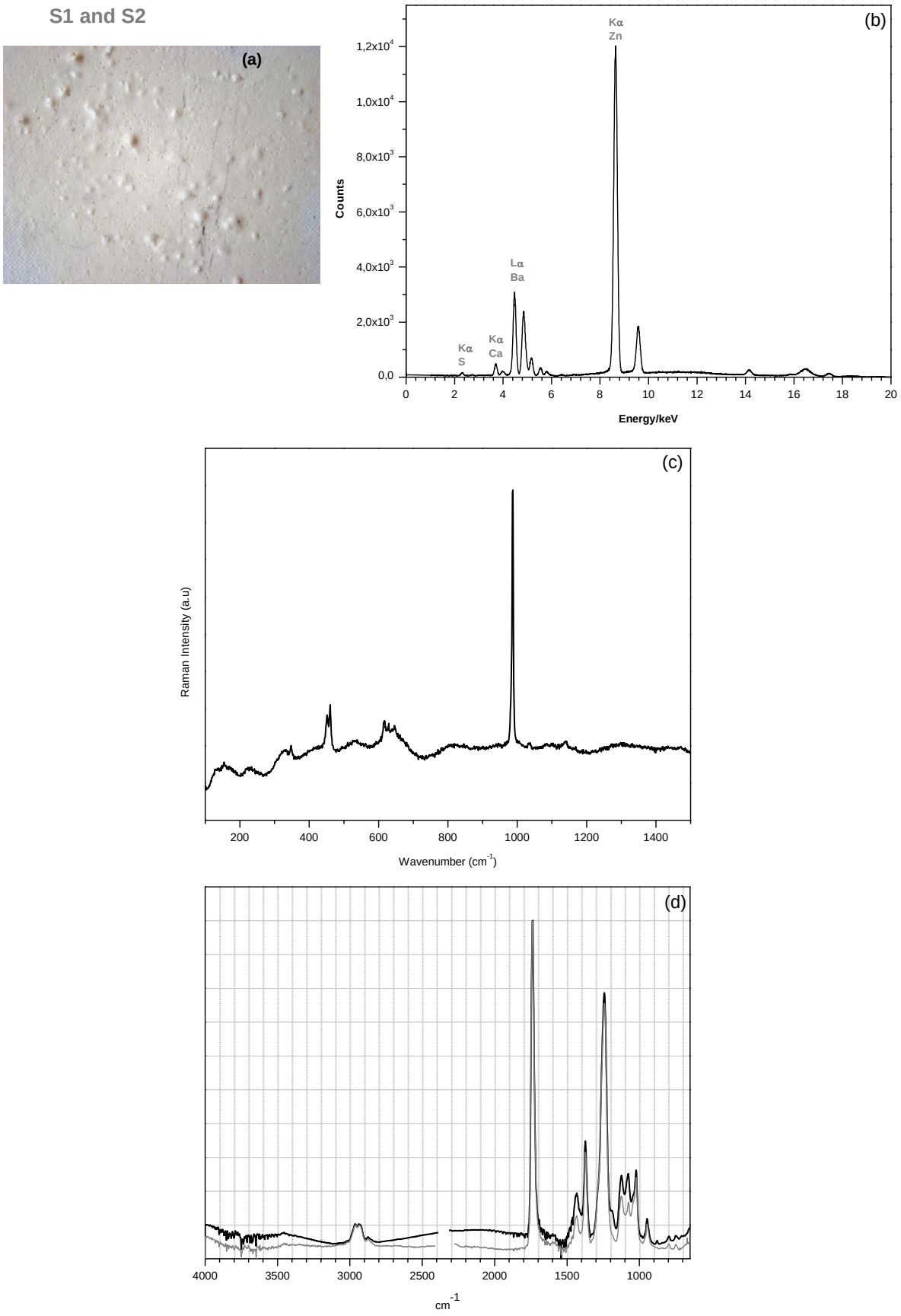


Fig.A5.35: (a) Detail of the white paint layer. (b) XRF spectrum (c) Raman spectrum of lithopone. (d) FTIR spectra of the PVAc binding medium from a white area (—) and a discolored area (—).

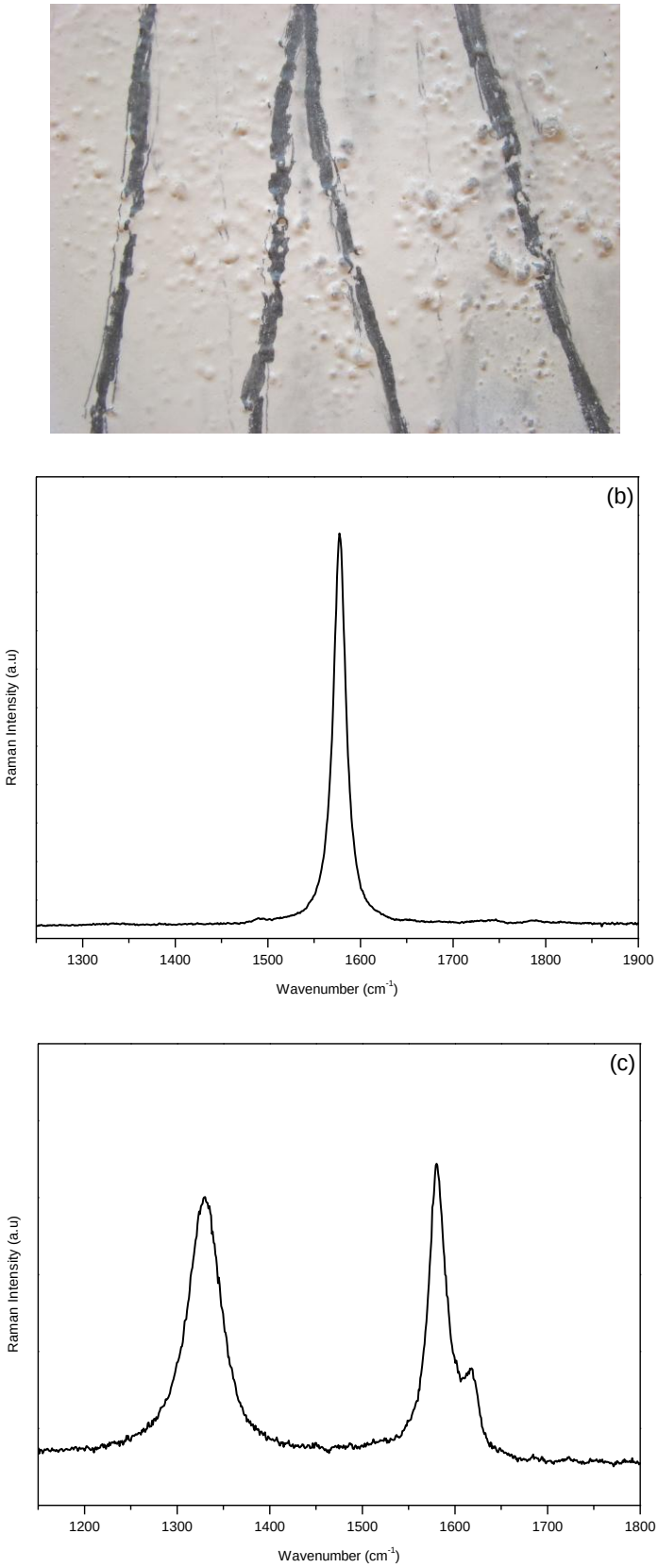


Fig.A5.36: (a) Detail of the drawing (b) and (c) Raman spectrum of pure graphite and graphite detected in the drawing.

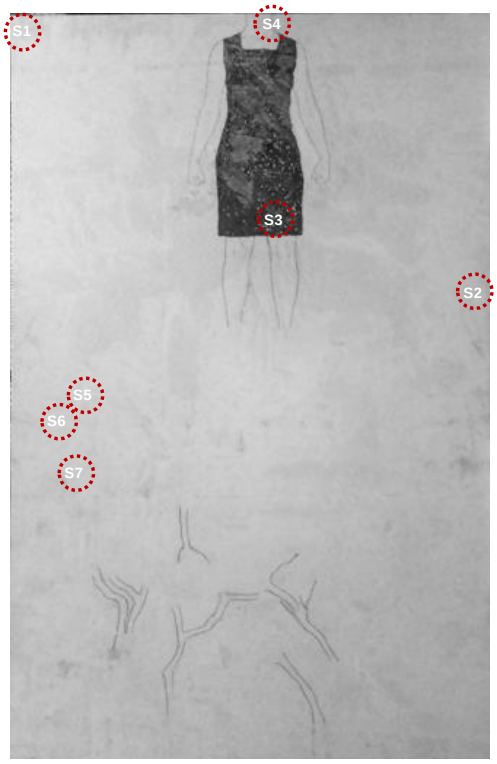


Fig. A5.37: Scheme with the location of the removed samples

Table A5.9: Summary of analytical results of *An involved story*

	Colour	Composition
S1	Dry pigment	Lithopone
S2	White paint layer	PVAc + Litophone+$CaCO_3$
S3	Black from the dress	Graphite
S4	Black drawing	Graphite
S5	White paint	PVAc + Litophone+$CaCO_3$
S6	Yellowed white paint	PVAc + Litophone+$CaCO_3$
S7	Very yellow paint	PVAc + Litophone+$CaCO_3$

S1, S6 and S7

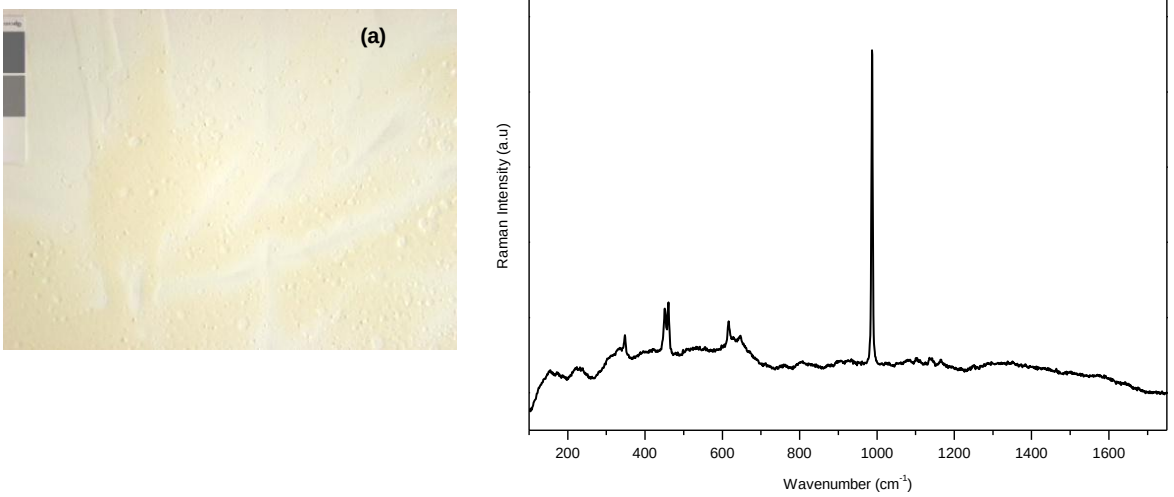


Fig.A5.38: (a) Detail of the white paint layer. (b) Raman spectrum of lithopone.

S3 and S4

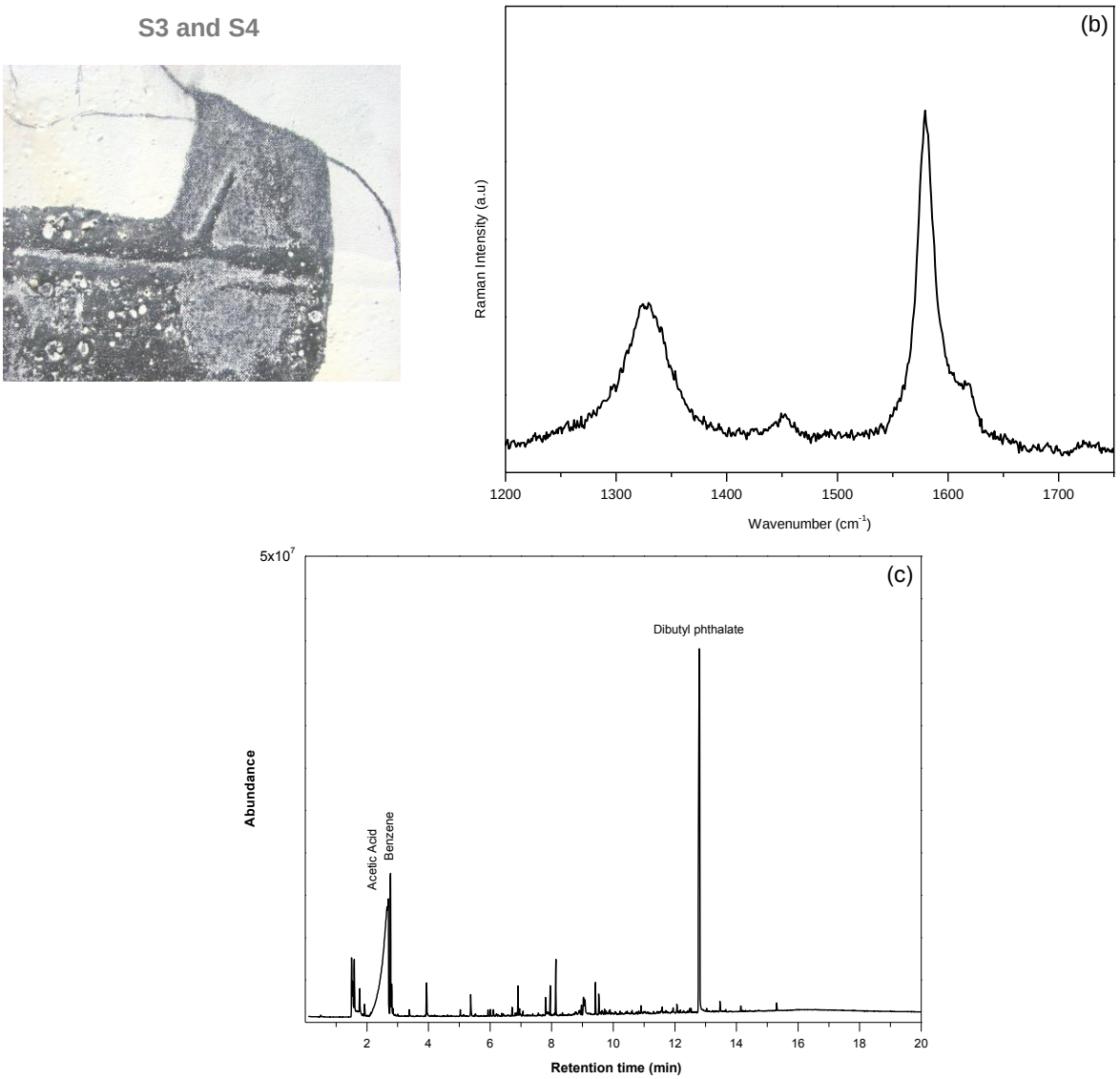


Fig.A5.39: (a) Detail of the drawing and black dress (b) Raman spectrum of graphite (c) White paint pyrogram showing a PVAc homopolymer.

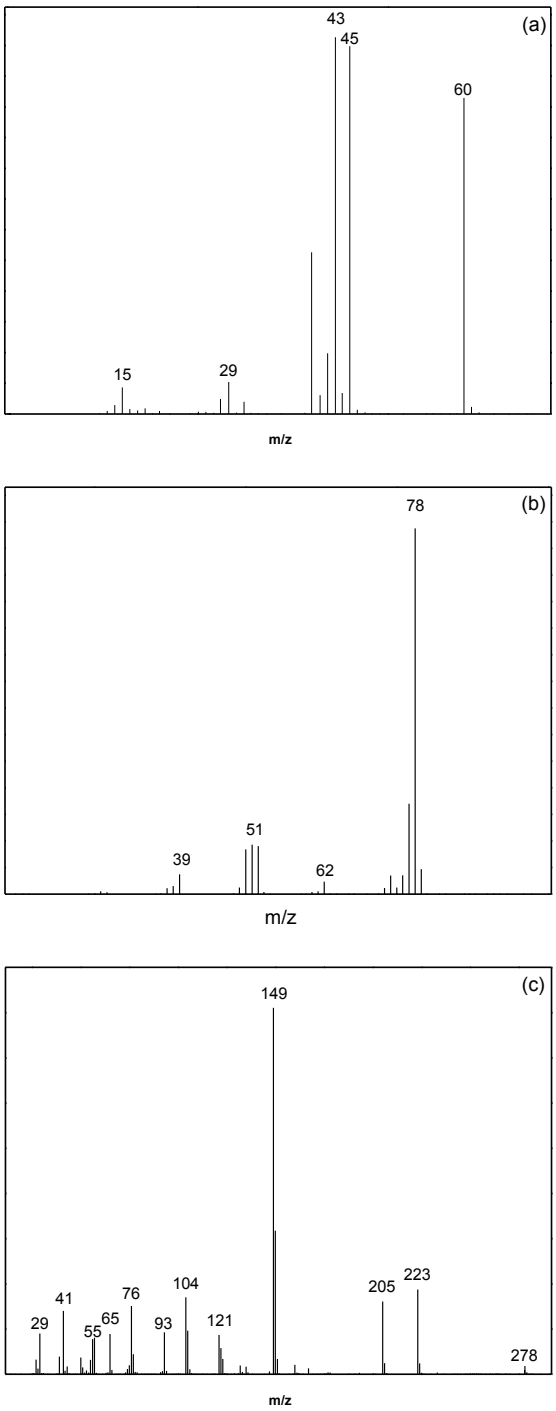


Fig. A5.40: Reference mass spectra taken from the pyrogram show in Fig A5.39 (a) mass spectrum of acetic acid (peak eluting at 2:73min) (b) mass spectrum from benzene (peak eluting at 2:78min) (c) mass spectrum of dibutyl phthalate (peak eluting at 12:80min).

Table A5. 10: Molecular species produced on the pyrolysis of the white sample from an *Involved Story*, the corresponding retention time, molecular weight and m/z values.

Molecular species	Retention time	Mw	m/z
Carbon dioxide	1:50	44	44
Water	1:53	18	18
2-Butene E	1:59	56	41,56,29
Acetone	1:77	58	43,58,15
1,3 – cyclopentadiene	1:93	66	66,39
Acetic Acid	2:70	60	60,43
Benzene	2:77	78	78, 51
1-Butanol	2:81	74	56,41,31
1-4 – ciclohexadiene	2:85	74	56,41,31
Acetic anhydride	3:38	102	43,15
toluene	3:94	92	91,65,39
Ethylbenzene	5:03	106	91,106
styrene	5:37	104	104,78,40,51
2-propenyl benzene	5:93	118	117,91
Camphene?	6:01	136	91,121,79,107,79
benzaldehyde	6:11	106	106,77,51
2-propenyl-benzene	6:72	118	117,91
1-propenyl-benzene	6:90	118	117,91
phenyl ester acetic acid	6:96	136	94,43,136,39,66
ethylmethyl benzene	7:07	120	105,77,117,51
1,4 - dihydronaphthalene	7:81	130	130,115,64
1,2 - dihydronaphthalene	7:95	130	130,115
naphthalene	8:13	128	128
1-methyl-naphthalene	8:97	142	142,115
1,2 - benzene dicarboxylic acid	9:04	166	104,76,50,148,117
1-methyl-naphthalene	9:08	142	142,115
Butyl benzoate	9:42	178	105,123,77,56
biphenyl	9:53	154	154,76,51
Fluorene	10:90	166	166, 82, 39
stilbene	11:59	180	180,165
9,10 - dihydro-phenanthrene	11:94	180	180,165
9-methylene - 9H-fluorene	12:07	178	178,76
Dibutyl phthalate	12:80	278	149,205,57,104
2-phenyl naphthalene	13:03	204	204,101
1-octadecamine, N, N - dimethyl	13:47	297	297,48
butyl 2-ethylhexyl ester phthalic acid	14:14	334	149, 223
mono 2-ethylhexyl phthalate	15:31	278	149, 167, 57,279

Table A5. 11: Molecular species produced on the pyrolysis of a yellowed white paint sample from an *Involved Story*, the corresponding retention time, molecular weight and m/z values.

Molecular species	Retention time	Mw	ion
Carbon dioxide	1:50	44	44
water	1:53	18	18
E-2-butene	1:59	56	41,56,29
Acetone	1:76	58	43,58,15
1,3 - cyclopentadiene	1:93	66	66,39
Acetic Acid	2:69	60	60,43
Benzene	2:77	78	78, 51
1-Butanol	2:80	74	56,41,31
1-3 - methyl-1,3 - cyclopentadiene	2:85	80	79,51,39,65
Acetic anhydride	3:38	102	43,15
toluene	3:94	92	91,65,39
Ethylbenzene	5:03	106	91,106
styrene	5:37	104	104,78,40,51
2-propenyl benzene	5:93	118	117,91
Propylbenzene	6:02	120	91,120,65
benzaldehyde	6:11	106	106,77,51
1-propenyl-benzene	6:72	118	117,91
Indene	6:90	116	116,89
phenyl ester acetic acid	6:96	136	94,43,136,39,66
acetophenone	7:07	120	120,105,77
1,4 - dihydronaphthalene	7:81	130	130,115,64
1,2 - dihydronaphthalene	7:95	130	130,115
naphthalene	8:13	128	128
2-methyl-naphthalene	8:97	142	142,115,71,129
phthalic anyhdride or, 1,2 - benzene carboxylic acid	9:05	166	104,76,50,148
1-methyl-naphthalene	9:08	142	142,115
Butyl benzoate	9:42	178	105,123,77,56
biphenyl	9:53	154	154,76,51
fluorene	10:90	166	166, 82, 39
stilbene	11:59	180	180,165
9-methylene - 9H-fluorene	12:07	178	178,76
Dibutyl phthalate	12:80	278	149,205,57,104
2-phenyl-naphthalene	13:03	204	204,101
butyl 2-ethylhexyl ester phthalic acid	14:14	334	149,223
mono 2-ethylhexyl phthalate	15:31	278	149, 167, 57,279

5.10. Inadequate Readings (Identity of anyone), private collection, 2004

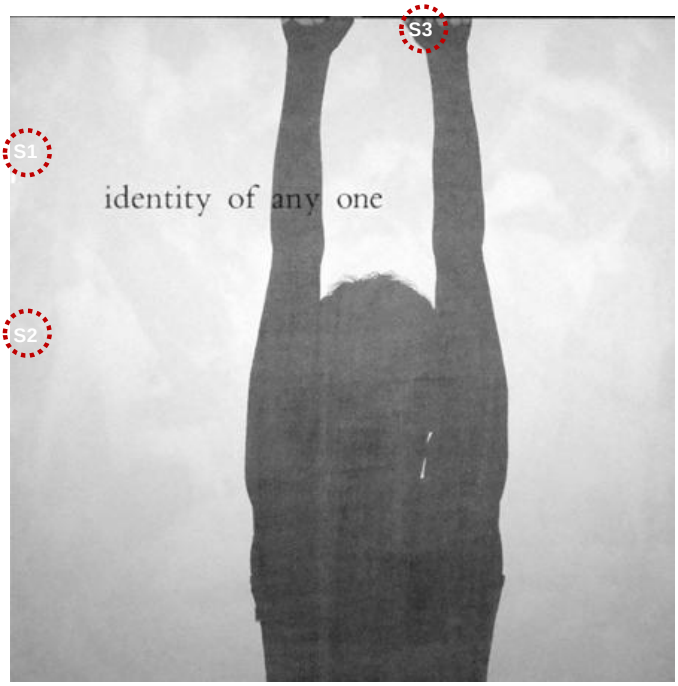


Fig. A5.41: Scheme with the location of the removed samples

Table A5.12: Summary of analytical results of *Inadequate Readings (Identity of anyone)*

	Colour	Composition
S1	White paint layer (mate)	PVAc + lithopone, $CaCO_3$
S2	White paint layer (cetin)	PVAc + lithopone, $CaCO_3$
S3	Black from the figure	P(VAc-E-VC) + Carbon black

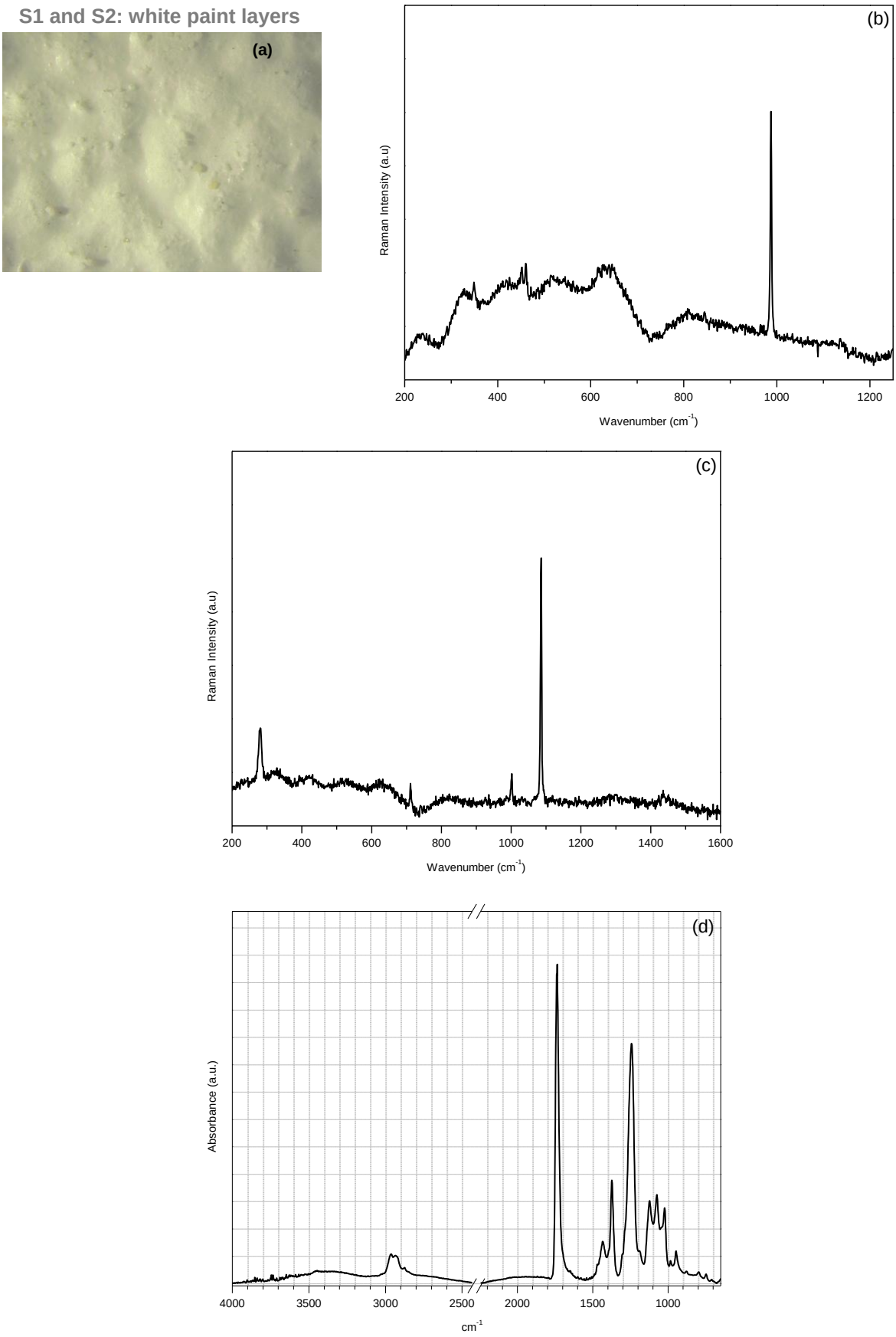


Fig.A5.42: (a) Detail of the white paint layer. (b) Raman spectrum of lithopone. (c) Raman spectra of $CaCO_3$ (d) FTIR spectrum of the PVAc binding medium and $BaSO_4$.

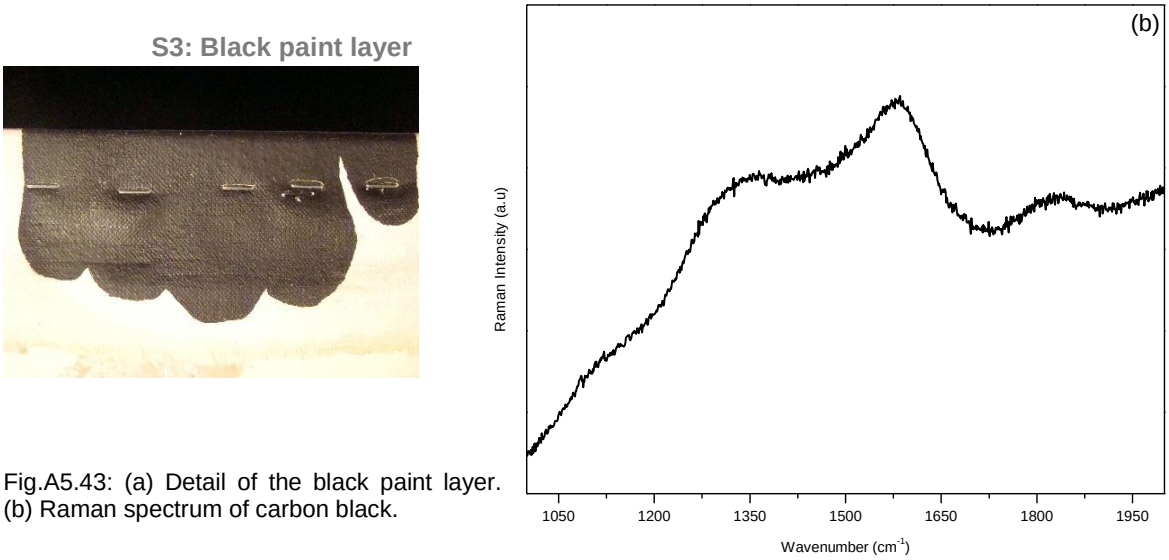


Fig.A5.43: (a) Detail of the black paint layer. (b) Raman spectrum of carbon black.

5.11. *Helder*, 2008 (FCG-CAM)

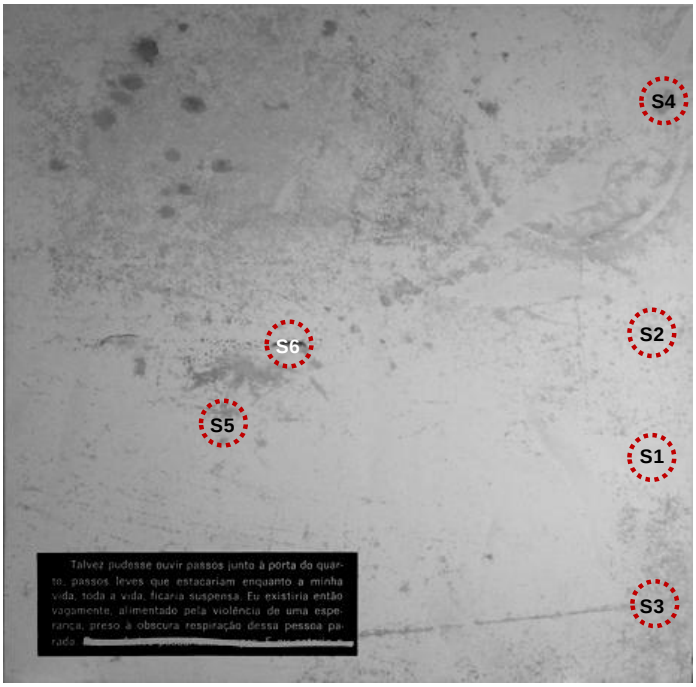
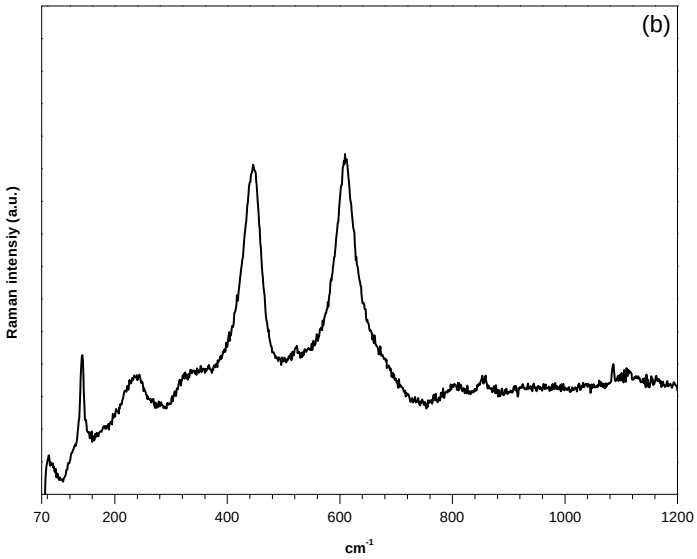


Fig. A5.44: Scheme with the location of the removed samples

Table A5.13: Summary of analytical results of *Hélder*

	Colour	Composition
S1	From the margin with all the layers	Top layer: Acrylic + PVAc + $CaCO_3$
S2	Satin white paint layer	PVAc + Acrylic +$CaCO_3$
S3	Matte white paint layer	PVAc + Titanium dioxide (rutile)
S4	Yellow paint layer	Acrylic + $CaCO_3$ + Rutile + organic pigment?
S5	Grey paint	$CaCO_3$ +Rutile + a little of Carbon Black + Mars Red



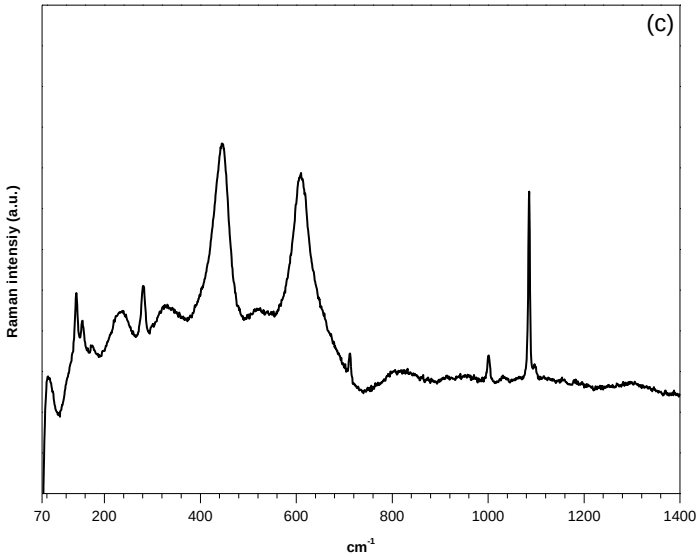
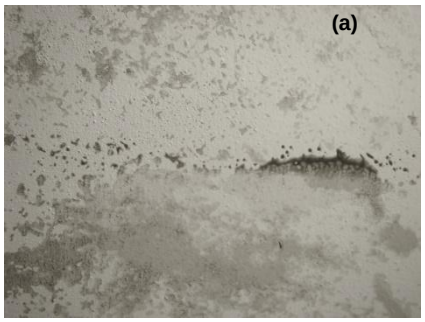


Fig.A5.45: (a) Detail of the white paint layers, with the satin layer on the left side and the matt layer on the right side (b) Raman spectrum of the satin white paint layer (c) Raman spectrum of the matt white paint.



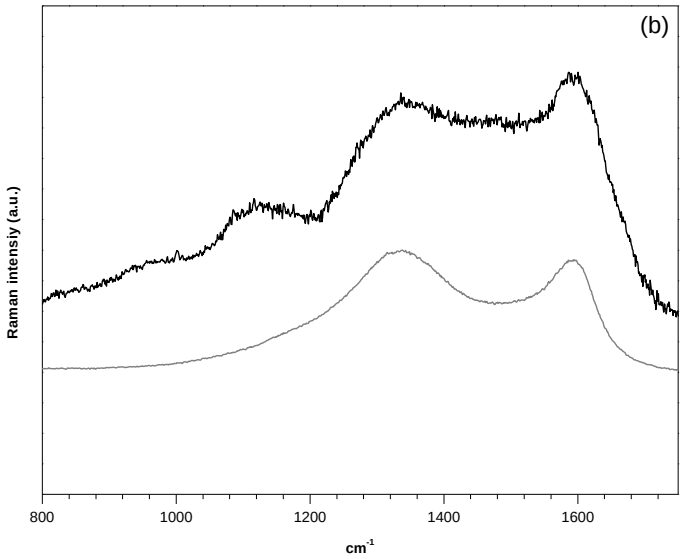
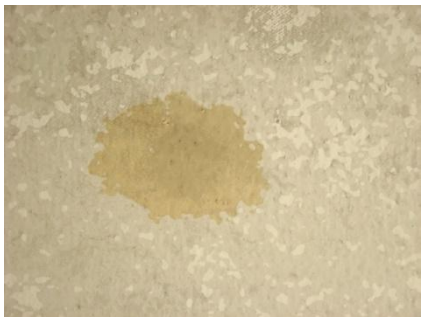
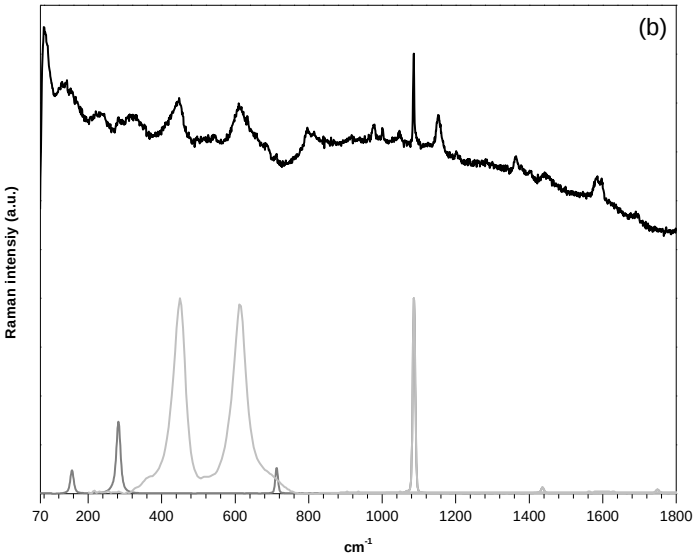


Fig.A5.46: (a) Detail of the grey abstract motifs (b) Raman spectra of carbon black found in the paint sample (—) and of a reference spectra of carbon black (—)





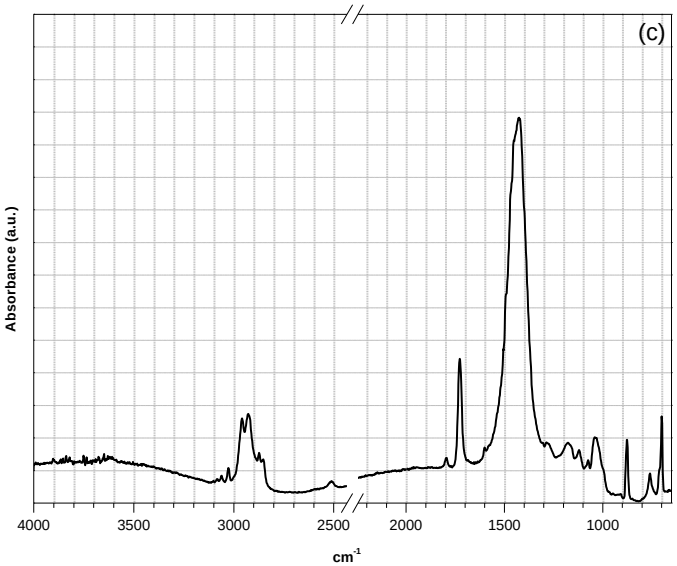


Fig.A5.47: (a) Detail of the yellow paint (b) Raman spectra of the paint sample (—), a calcite reference spectra (—) and a TiO_2 rutile reference spectra (—)
(c) FTIR spectrum of the acrylic binder and calcium carbonate

Table A5.14: Wavenumber of the main vibrations of the vinyl binder found in the case studies

	Leftover		***I don´t want to…***		***Wasting my time…***			***Belém***	
	White	*Yellowed*	White	*Yellowed*	White	*Yellowed*	Black	White	*Yellowed*
vCH	2964-63	*2963-60*	2964-60	*2963-61*	2963-60	*2963*	2966-64	2963-60	*2962-60*
	2936-33	*2936-30*	2933-26	*2934-32*	2933-30	*2933-32*	2930-35	2939-33	*2933-30*
	2875-72	*2875*	2872-71	*2873*	2875-72	*2875*	2875-74	2875-74	*2875-72*
vC=O	1735	*1735*	1737-36	*1737-36*	1738-35	*1735*	1736-35	1739-38	*1739-35*
δCH	1433-30	*1433-30*	1436-34	*1435*	1433-30	*1433-30*	1436-33	1434-33	*1434-33*
	1376-75	*1375-72*	1375-73	*1374-73*	1375	*1375-72*	1374-72	1374-72	*1373-72*
vCO	1241	*1244-41*	1242-41	*1243*	1244	*1244-41*	1242-41	1243-41	*1243-41*
vCC	1123-22	*1123-22*	1122	*1123*	1122	*1123-22*	1121-19	1124-22	*1124-22*
δCH (ring)	1077-76	*1076-74*	1077-75	*1075*	1077-76	*1076-74*	1074-73	1077	*1077-75*
vCC	1022-21	*1024-21*	1025-23	*1023*	1022	*1024-21*	1025-23	1023-22	*1023-22*
vCO	948-6	*949*	947-6	*947-6*	948-5	*949*	947	948-7	*947*
—	796	*796*	796	*796*	796	*796*	796	796-5	*796*

Table A5.14 (cont.): Wavenumber of the main vibrations of the vinyl binder found in the case studies

	Pintura Cega			***Frozen Leopard***		
	White	*Yellowed*	Black	White	*Yellowed*	Red
vCH	2962-58	*2964-62*	2967-63	2961	*2962-61*	2963-62
	2935-24	*2933-25*	2930-27	2929-28	*2929-26*	2930-29
	2875-69	*2875-70*	2875-66	2873-72	*2874-72*	2875-73
vC=O	1737-36	*1737-36*	1735	1736	*1739-37*	1737-35
δCH	1435-33	*1435-34*	1433	1433-31	*1434-33*	1433
	1373	*1373-72*	1372	1375-73	*1373*	1373-72
vCO	1242-41	*1242-41*	1241-38	1242-41	*1242-41*	1241-38
vCC	1124-23	*1124-23*	1122	1121	*1122*	1123-21
δCH (ring)	1078-74	*1076-74*	1077-73	1076	*1078-74*	1076
vCC	1023	*1023-22*	1025	1023-22	*1023*	1023-22
vCO	947	*947*	948	947-6	*947*	947
—	796	*795*	796	798-6	*796*	797

Table A5.14 (cont.): Wavenumber of the main vibrations of the vinyl binder found in the case studies

	An involved story		***Inadequate Readings***	***Helder***
	White	*Yellowed*	White	*White*
vCH	2963-60	*2963-59*	2966-63	*2964-59*
vCH	2936-34	*2937-27*	2936-30	*2934-35*
vCH	2875-74	*2875-72*	2878-75	*2874-76*
vC=O	1737-36	*1737*	1735	*1740-36*
δCH	1429-32	*1433-32*	1433-30	*1436-32*
δCH	1376-73	*1374-73*	1372-75	*1376-73*
vCO	1243-42	*1242-41*	1241	*1243*
vCC	1124	*1124-23*	1122	*1124-23*
δCH (ring)	1076	*1077-75*	1077-74	*1074*
vCC	1023	*1023-22*	1024-22	*1023*
vCO	947	*947*	948	*947*
—	795	*796-5*	796	*795*

Table A5.15: Infrared absorptions normalized for the C=O stretching for the vinyl binder present in the case-studies.

	Leftover		***I don´t want to go***		***Wasting my time…***		***Belém***	
	White	*Yellowed*	White	*Yellowed*	White	*Yellowed*	White	*Yellowed*
vCH	0.10± 0.02	*0.08± 0.01*	0.06± 0.01	*0.06± 0.00*	0.07± 0.01	*0.07± 0.00*	0.09± 0.01	*0.09± 0.00*
vCH	—	*0.08± 0.01*	0.07± 0.00	*0.06± 0.00*	0.08± 0.01	*0.07± 0.00*	—	*0.09± 0.01*
vCH	—	—	0.04± 0.01	—	—	*0.04± 0.00*	—	*0.05± 0.00*
vC=O	1.00	*1.00*	1.00	*1.00*	1.00	*1.00*	1.00	*1.00*
vCO	0.78± 0.02	*0.79± 0.02*	0.78± 0.04	*0.73± 0.07*	0.86± 0.13	*0.74± 0.03*	0.78± 0.01	*0.79± 0.02*

Table A5.15 (cont.): Infrared absorptions normalized for the C=O stretching for the vinyl binder present in the case-studies.

	Pintura Cega			***Frozen Leopard***		
	White	*Yellowed*	Black	White	*Yellowed*	Red
vCH	0.08± 0.01	*0.08± 0.01*	0.10± 0.01	0.08± 0.00	*0.09± 0.01*	0.11± 0.02
	0.09± 0.01	*0.09± 0.01*	0.11± 0.01	0.09± 0.00	*0.10± 0.01*	0.12± 0.02
	—	—	0.06± 0.01	0.05± 0.00	—	—
vC=O	1.00	*1.00*	1.00	1.00	*1.00*	1.00
δCH	—	—	—	—	—	—
vCO	0.76± 0.01	*0.76± 0.01*	0.81± 0.04	0.78± 0.04	*0.78± 0.04*	0.90± 0.04
vCC	—	—	—	—	—	—
δCH (ring)	—	—	—	—	—	—

Table A5.15: (cont.): Infrared absorptions normalized for the C=O stretching for the vinyl binder present in the case-studies.

	An involved story		***Inadequate Readings***	***Helder***
	White	*Yellowed*	White	White
vCH	0.010± 0.01	*0.09± 0.01*	0.10± 0.01	0.08± 0.01
	0.10± 0.01	*0.10± 0.01*	0.10± 0.01	0.07± 0.01
	0.06± 0.01	*0.05± 0.00*	0.06± 0.01	0.06± 0.01
vC=O	1.00	*1.00*	1.00	1.00
δCH	—	—	—	0.32± 0.00
vCO	0.83± 0.04	*0.77± 0.01*	0.76± 0.02	0.73± 0.00
vCC	—	—	—	0.17± 0.00
δCH (ring)	—	—	—	0.15± 0.00

5.12. Analyzes of VeoVa copolymers: paintings from the 80's

Although in previous work infrared spectroscopy was used to distinguish between PVAc from PVAc-VeoVa copolymers [2,151] in this case the results were not straightforward. FTIR spectra obtained from reference materials (samples provided by *Resiquímica*) of know compositions (c.70% PVAc) were compared with the values present in the literature [1] and with the paints used by Sarmento. Calculation of absorbance ratios from the infrared spectra were calculated according to previous methods [151], however the results were not conclusive.

In order to distinguish between the homopolymer and the copolymer two spectral ranges have to be observed: 3000-2800cm^{-1} and the range 1200-1000cm^{-1}. In PVAc the methyl stretching at c. 2976cm^{-1} is less intense than the corresponding vibration at 2926cm^{-1}. In the case of the copolymer the relative intensities of these two bands changes and there is also the appearance of the band at c.2870cm^{-1}. However if there is also an external plasticizer as it seems that the distintion between the homopolymer and the copolymer is no longer straightforward. The vibration due to CH_3 groups present in the plasticizer will make both spectra very similar in this area. In the 1200-1000cm^{-1} range one can look for differences in the shape of the band at 1124cm^{-1}. This is more intense for the copolymer than for the homopolymer; and broader than in the homopolymer emulsion. Nevertheless this is not a reliable system to establish if a copolymer was used. For instance *Imofan* emulsion was identified by Py-GC/MS as a PVAc-VeoVa but, the FTIR spectra is very similar to the studied homopolymer emulsions. The fact that *Imofan* contains additionally DiBP as an external plasticizer might account for the similarities between copolymer and homopolymer emulsions spectra.

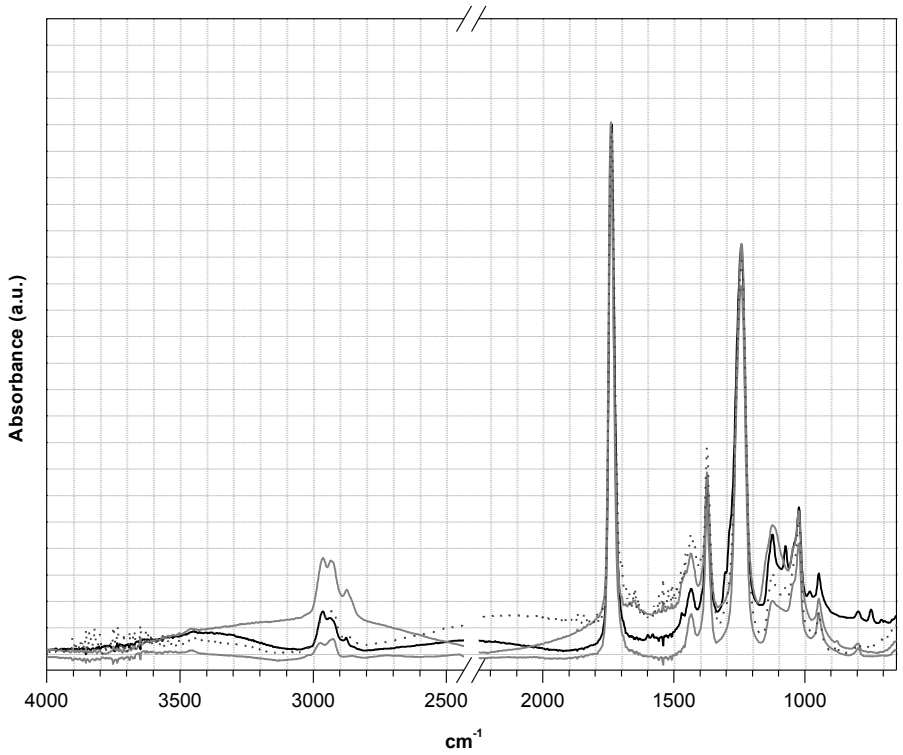


Fig. A5.49 – Infrared spectra of PVAc emulsion (*Vulcano V7* with DiBP) (—), PVAc (applied from solution) (—), PVAc-VeoVa emulsion (*Resíquimica DM22*) (—) and *Imofan* Av44-11 (…)

Table A5.16: Infrared absorptions normalized for the C=O stretching for the vinyl binders homo and co-polymers.

		PVAc		*V7*	*Sabu*	*Bizonte*	*Imofan*
vCH	2972	0.05±0.00	2964-1	0.09±0.01	0.10±0.01	0.15±0.02	0.07±0.00
vCH	2927	0.06±0.00	2939-33	0.08±0.01	0.10±0.01	0.13±0.02	0.08±0.01
vCH	—	—	2878-75	—	—	—	0.04±0.00
vC=O	1735	1.00	1735	1.00	1.00	1.00	1.00
δCH	1433	—	1433	—	0.13±0.01	—	—
δCH	1372	0.11±0.01	1372	0.32±0.01	0.32±0.00	0.40±0.02	
vCO	1241	0.77±0.06	1244-38	0.76±0.01	0.75±0.01	0.76±0.01	0.73±0.02
vCC	1122	0.14±0.02	1123-22	0.19±0.03	0.21±0.00	0.29±0.03	0.14±0.02
δCH (ring)	—	—	1076-74	—	0.18±0.00	0.27±0.03	0.11±0.02
vCC	1022	—	1022	0.25±0.02	0.26±0.01	0.33±0.03	0.23±0.03
vCO	950	—	950-46	—	0.12±0.01	—	0.08±0.00

Table A5. 17: Infrared absorptions normalized for the C=O stretching for several Veo-VA emulsions

		DH		DM23	DM21	DM22	DM510	DM9725
vCH	2970	—	2964-57	0.15±0.02	—	0.14±0.01	0.15±0.01	—
vCH	2930	—	2933-30	0.15±0.02	—	0.14±0.01	0.17±0.01	—
vCH	—	—	2878-75	0.10±0.01	—	0.08±0.01	0.11±0.01	—
vC=O	1735	1.00	1741-35	1.00	1.00	1.00	1.00	1.00
δCH	1430	0.13±0.02	1436-33	0.15±0.00	—	—	0.12±0.01	—
δCH	1372	0.34±0.01	1372	0.34±0.00	0.34±0.02	0.32±0.02	0.33±0.01	0.33±0.04
vCO	1241	0.77±0.02	1241	0.80±0.01	0.80±0.02	0.79±0.02	0.79±0.02	0.80±0.04
vCC	1122	0.16±0.01	1129-22	0.22±0.02	0.22±0.04		0.19±0.01	—
vCC	1022	0.27±0.02	1022-21	0.28±0.02	0.27±0.04	0.25±0.03	0.29±0.01	—

Table A5. 18: Wavenumbers as analyzed by FTIR of the vinyl binder found in *52* and *Salto*

	52					*Salto*			
	Black	*Red*	*White yellowish*	*White*	*Yellow*	*White*	*Blue*	*Black*	*Red*
vCH	2968	2957	2963	2964	2965	2961	2970	2960	2964
vCH	2935	2937	2930	2934	2936	2935	2933	2933	2935
vCH	2873	2874	2874	2874	2874	2874	2870	2875	2875
vC=O	1739	1736	1739	1740	1738	1740	1736	1740	1737
δCH	1434	1434	1432	1428	1434	1428	1431	1430	1430
δCH	1374	1373	1373	1375	1374	1375	1373	1374	1375
vCO	1243	1239	1243	1242	1243	1243	1244	1242	1242
vCC	1119	—	1124	1123	1123	1121	—	—	1122
δCH (ring)	1073	—	1077	1075	1075	1076	—	—	1046
vCC	1024	—	1023	1024	1024	1025	—	1025	1023
vCO	947		947	947	947	984	—	—	—
	798	797	795	—	796	947	—	947	947
	749	753	747	—	747	—	799	796	796

FTIR spectra of the painting *52* proved not to be enough to determine if a homopolymer or, a copolymer emulsion was used. The 1150-1000cm^{-1} interval is in most of the samples masked by the presence of white fillers. Only the black paint spectrum has no influence in this area. However the band at 1074cm^{-1} probably due to the presence of an external plasticizer influences the shape and relative intensity of the bands at that interval. Between 3000-2800cm^{-1} three bands due to CH

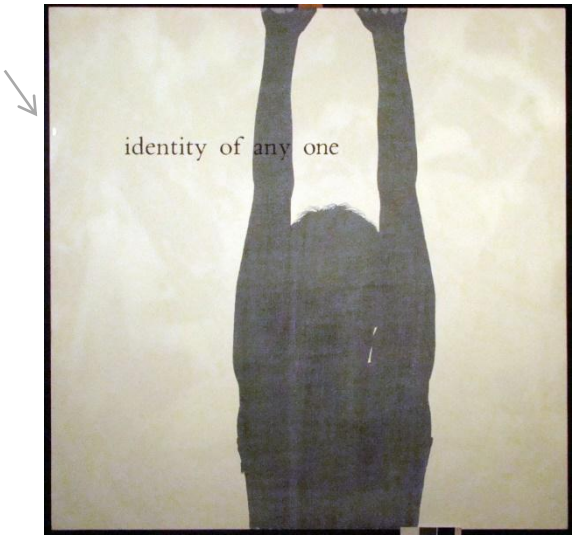
stretching appear in all the samples analyzed however they could be either from the VeoVa component or, due to an external plasticizer.

The use of a copolymer had to be verified by Py-GC/MS. The same difficulty was found in the FTIR spectra interpretation as all the samples also contained DBP except for the blue paint. However the shape of the vCH bands in this paint is similar to a PVAc free of additives and not to a VeoVa copolymer. The 1150-1000cm^{-1} area is masked by the ultramarine blue.

Salto seems to be impregnated by the glue used to secure the paper to a textile support which makes infrared spectra difficult to interpret. All the spectra from the paint layers show absorbance bands that are present in the FTIR spectra of the glue itself. Nevertheless a vinyl versatate copolymer was detected on the white and red paint layers by Py-GC/MS. Several PVAc-VeoVa emulsions were analyzed by FTIR in order to establish the differences. The 1150-1000cm^{-1} interval seems to be characteristically different for VeoVa copolymers.

Appendix VI: Treatment of *Inadequate Readings (Identity of anyone)*, 2003

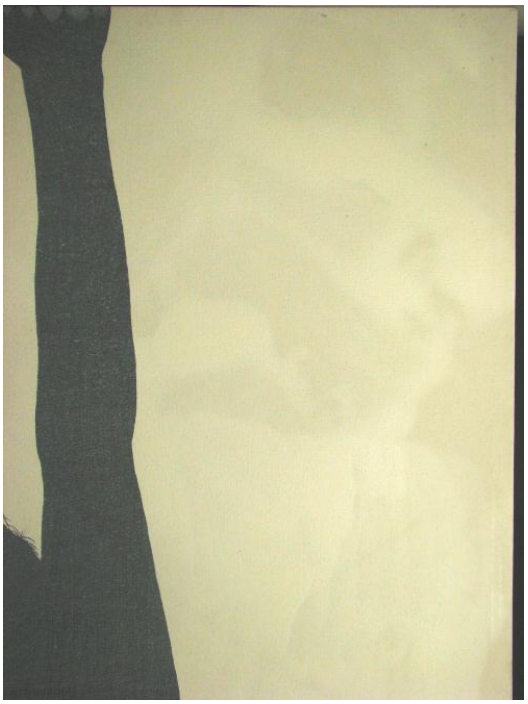
Research information was put in to practice as the treatment of one of Sarmento's works was requested by the artist. *Inadequate Readings(Identity of anyone)* painted in 2004 had suffered severe local damage during storage. After being exhibited and during storage and/or transportation a fragment of glass got stuck on the paint's surface. The damage was discovered when the staff from a Portuguese art gallery removed the plastic with which the painting had been wrapped. After unsuccessful attempts to remove mechanically the piece of glass, the artist approached the us for a solution. After a first examination a decision was made to transport the painting into the Department where a more comprehensive examination could be done and a conservation treatment could be carefully planned and carried out. Thorough knowledge of the materials and techniques used by Sarmento was invaluable to set a treatment strategy. Mock-ups for treatment trials created with Sarmento's materials avoided having to try treatment methodologies in the painting itself.



Figs. A6.1 and A6.2 – Front and back of *Inadequate Readings (Identity of anyone)* (2004). The painting as a square format of 120cmx120cm and is 6cm thick. The piece of glass is located at the left margin, upper part (indicated by the arrow).

Observation of the paint surface with a microscope and UV light revealed that two white paint layers were present. It seems that Sarmento applied the white background, drawed the black figure in pencil, filled it out with black paint and finally poured a very liquid white paint over the composition. According to the μFTIR results the two white paints were made with a poly(vinyl acetate) binding medium. The white color is provided by lithopone and calcium carbonate is present as the filler. The infrared spectra obtained for the black paint is very similar to the reference spectra of the PVAc copolymer based emulsion *Sabu* black indicating that the artist might have used this brand of paint.

The white paint layers cover the cotton canvas surface heterogeneously and the canvas texture is still largely perceptible underneath the paint. (Fig. A6.3 and A6.4)



Figs. A6.3 and A6.4 – Details of *Inadequate Readings* in normal (right) and raking light (left) showing the heterogeneous thickness and distribution of the white background paint.

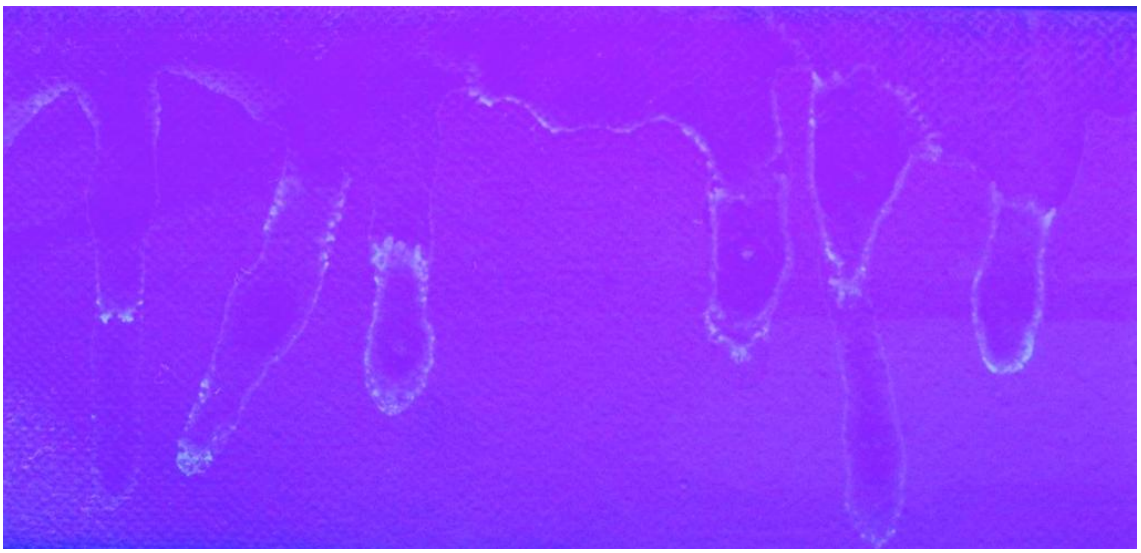


Fig. A6.5 - Detail of the margin on the back of the painting under UV light. The examination made evident the presence of a second paint layer that runs over the painting margins.

Fig.A6.6. – Detail of the painting with the glass stuck on the paint's surface.

Unfortunately, the glass seems to have compressed the paint surface. Two circumstances have contributed to the severity of the problem.

First the low T_g of these paints as indicated by the DSC analysis (between 10 and 16.2ºC). Secondly, the glass is in the worst possible place, near the margin where the wooden stretcher is completely flat underneath. Fig. A6.7. depicts the profile of the structure and the position of the glass. Images taken in the microscope reveal the level of damage that occurred on the surface and the suppleness of the paint following the pressure exerted during the damage.

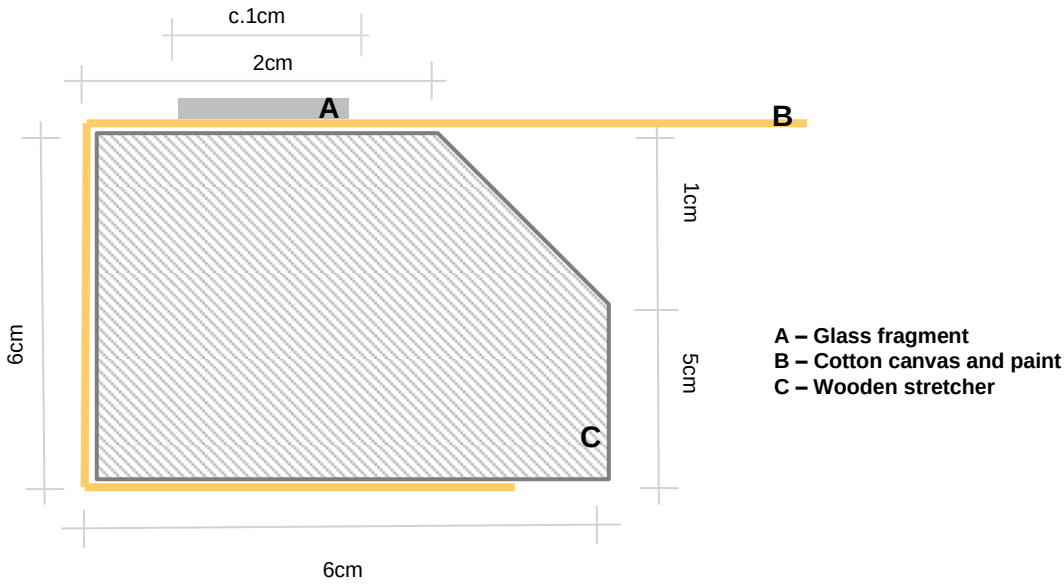
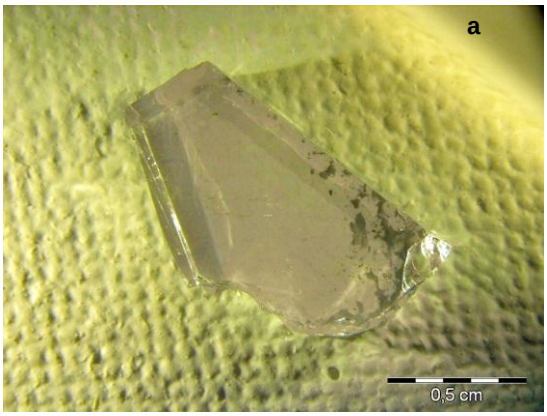
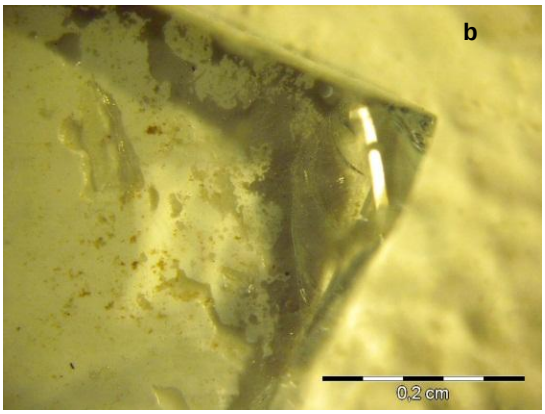


Fig.A6.7. – Scheme depicting the painting profile where the piece of glass was stuck to the paint's surface.





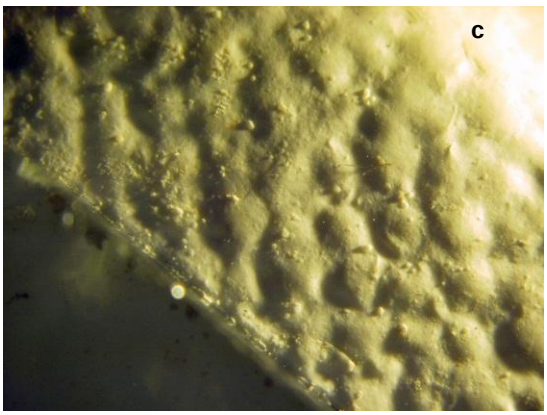


Fig. A6.8 – Details under the microscope. (a) The general view at 7x magnification shows that under the glass the paint surface is now a flat surface. (b) Zooming in using a magnification of 20x reveals that under a small area where the glass is not stuck to the surface the paint retains the texture of the canvas. (c) Using the same magnification but, under raking light there is evidence that sufficient pressure was exerted to make the glass compress the paint, so that around the glass margin a bulge of paint was formed.

Several mock ups were created in order to try diferent treatment strategies. White paint was applied over bare cotton canvas. The materials used were provided by the artist. The paint was made with 70% of white glue (*Vulcano V7*) plus 30% of *Cenógrafa* white and was apllied with a film applicator. Replicas of the stretcher profile were created so that any method tried could be applied later on the painting with a higher level of confidence. Pieces of glass of the same tchickness were cut to the same size and format as the one on the painting. These were stuck on the reproductions by applying heat on the paint (with a small air drier) and pressing the glass down on to the surface.

Literature review on conservation & restoration of contemporary art did not bring any new ideas. In fact to the best of our knowledge there was no published information regarding treatment of similar cases. Currently treatments on acrylic paintings tend to be minimal and seem to be limited to cleaning, consolidation and retouching of paintings.[152]

The treatment trials intended to take advantage of the known physical and chemical properties of vinyl emulsion paints. PVAc is a thermoplastic polymer which means that the macromolecules are two-dimensional linear chains that are not connected by covalent bonds. The paint will soften and flow when heated and will regain its hardness on cooling.This process should be able to be repeated several times. Research has showed that stiffness of PVAc based dispersions can be very sensitive to small differences of temperature (1ºC) when they are close to their glass

transition temperature.[86] As the temperature is raised the increase in the polymer specific volume is attributed to the formation of small holes or, voids in the system which collectively increases in size.[86] Therefore treatment options obvisouly involved slightly heating the surface with a gentle jact of air flow. Alternatively, if heating makes the surface tackier it could get the glass even more adhered. Therefore, the opposite condition, using cold (in this case with dry ice) could make the surface harder and help to remove the glass.

Fig.A6.9. – Mock-ups used for treatment trials. (a) White paint was applied on bare canvas. (b) Several replicas of the stretcher were cut in wod. (c) The paint reproductions were then stapled to the stretcher replicas and a glass fragment was glued on the paint layer. (d) mock-up ready for a treatment trial.

Besides the physical properties, chemical properties were also considered. Trials with water and with solvents intend to see if both could have a plasticizing effect on the paint and help in the detachment of the glass fragment. Vinyl and acrylic paints are theoretically insoluble in water after drying. However their formulation includes a complex array of additives. For example, coalescent solvents and freeze thaw agents that are expected to be released from the paint upon drying.[97] Others such as the surfactants, dispersants and thickeners are supposed to remain in the dried film.[97] These additives e.g. the surfactants might make the films moisture sensitive. Poly(vinyl alcohols) are often present in PVAc emulsions to serve as protective colloids [8] and they can be affected by water. Previous trials with immersions of unpigmented *Vulcano V7* in distilled water had caused blushing of the layer. Therefore, the affinity for water was expected to alter the

mechanical properties of the paint by eventually provoking a softening effect. In fact, acrylic emulsion paint films show a decrease in stiffness and an increase in elongation when exposed to moisture.[35] The authors believe there is increased flow of the polymer chains due to disruption of hydrogen bonding between components in the film and swelling increase the free volume. [35] As a previous test also showed that *Vulcano V7* can be affected by ethanol, this was included in the tests. Taking into account the solubility properties of other solvents towards PVAc it was decided that other solvents would most probably damage the paint. Tests done on the mock-ups demonstrated that the only efficient and visually safe method to be used was an alternate application of c.10minutes of cold (using dry ice) followed by c.10minutes of heat (soft warm air flow). Cyclical shrinkage (with cold) and expansion (with heat) of the paint while the glass physical state stays inert helped to gradually lossen adhesion and finally remove the glass without provoking further damage in the paint's surface.

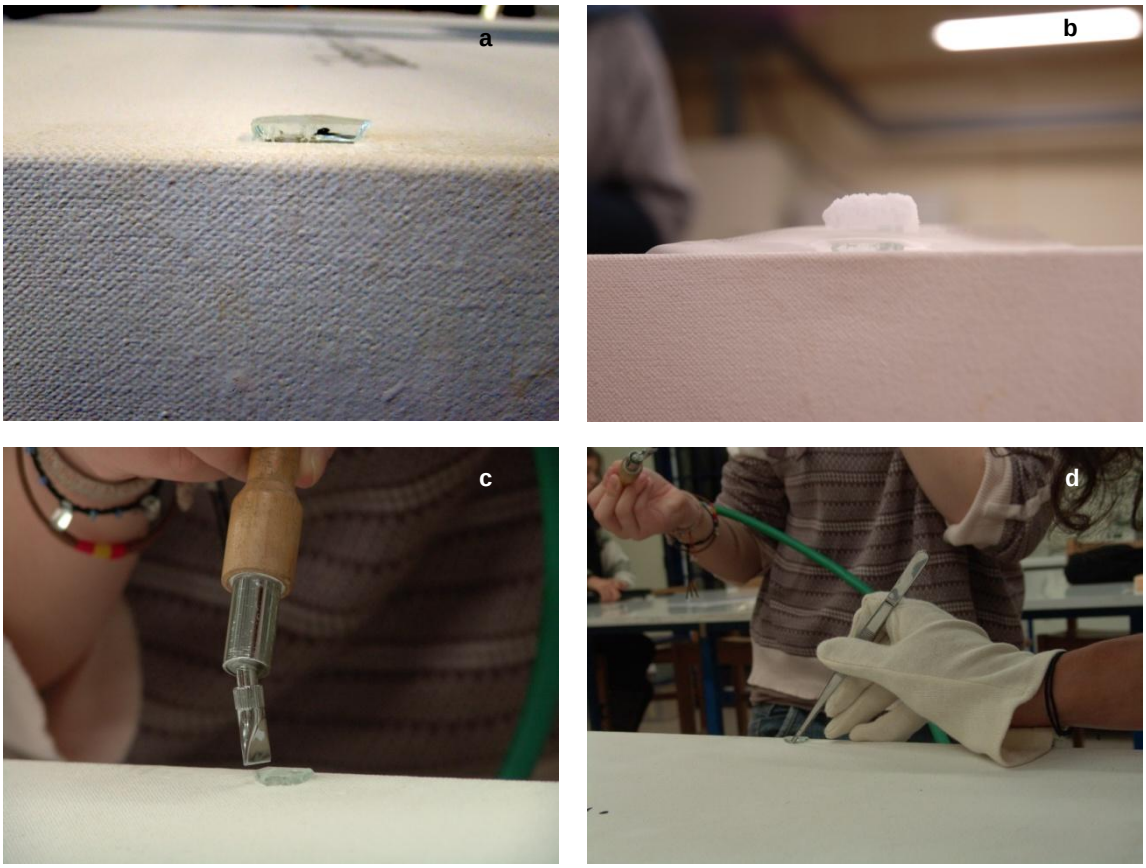


Fig.A6.10. – Treatment of *Inadequate readings (Identity of anyone)*. (a) Detail of the painting before treatment (b) Application of the dry ice using a melinex foil in between (c) Application of heat with an air jact (d) Trial for mechanical removal of the glass in between cycles of heat and cold.

As suspected during observation the painting texture imparted by the canvas on the paint was destroyed under the glass. Slight heating of the surface while simultaneously impressing the texture of a canvas on the surface was sufficient to re-create a more textured surface. This was achieved with a spatula to which a canvas of similar weave to the one used by the artist in this work was attached.

Fig.A6.11. – Details during and after treatment under the stereomicroscope (a) and (b) after the removal of the piece of glass, magnification 7x and 16x respectively (c) and (d) After imparting a canvas texture on the paint's surface, magnification 10x and 16x respectively (e) The method used for re-creating the weave texture in the damaged surface.

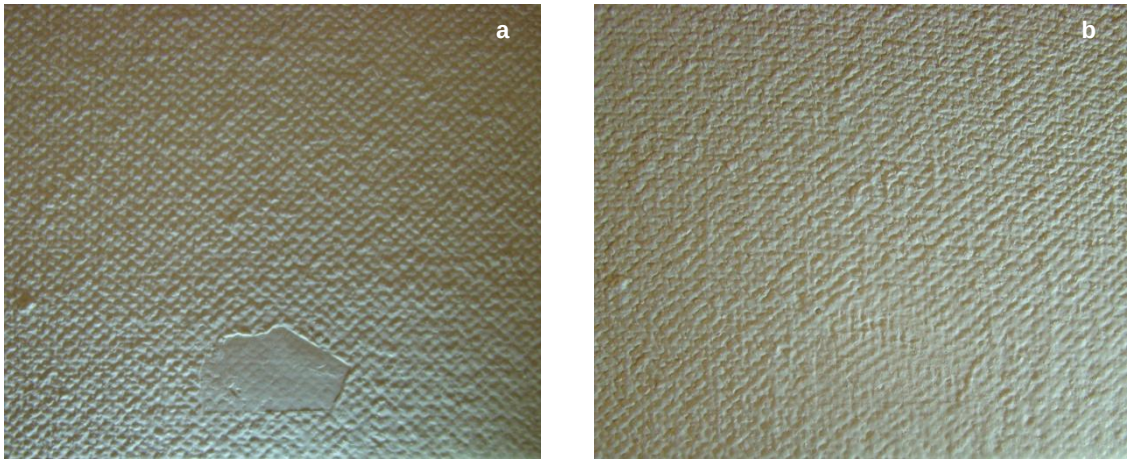


Fig.A6.12. – Details of the paint's surface before (a) and after treatment (b) under raking light.

A note on the results obtained with the solvents used in the mock-ups should be made. Both ethanol and water were apllied with a soft and small brush along the edges of the glass. The purpose was to see if the solvent would difuse between the glass and the paint surface softening the paint and facilitating the removal of the glass. In both cases a piece of melinex sheet was used to keep the solvents from evaporating too fast and was only removed after no visual evidence of solvent in the surface was found. In both solvents no positive results were obtained regarding the treatment. However after solvent evaporation the surface seemed brighter and translucid sugestting the dissolution and migration of some of the paint's additiives. This results triggered further analysis to explain the process and the results can be seen in Part II, Cleaning of synthetic paints)

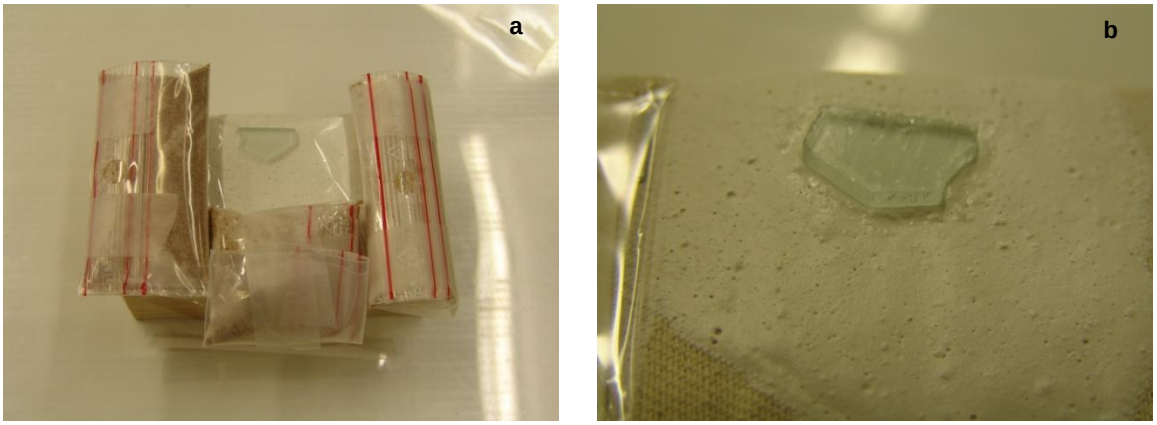


Fig.A6.13. – Mock-up used to test water. (a) After application of ethanol with a soft brush the mock-up was covered with a sheet of melinex to avoid the quick evaporation of the solvent. (b) after solvent evaporation a brighter surface could be seen where the solvent had been applied.

Appendix VII: Natural aging, discoloration of Sarmento's paints

7.1. Materials characterization: Canvas used by Sarmento

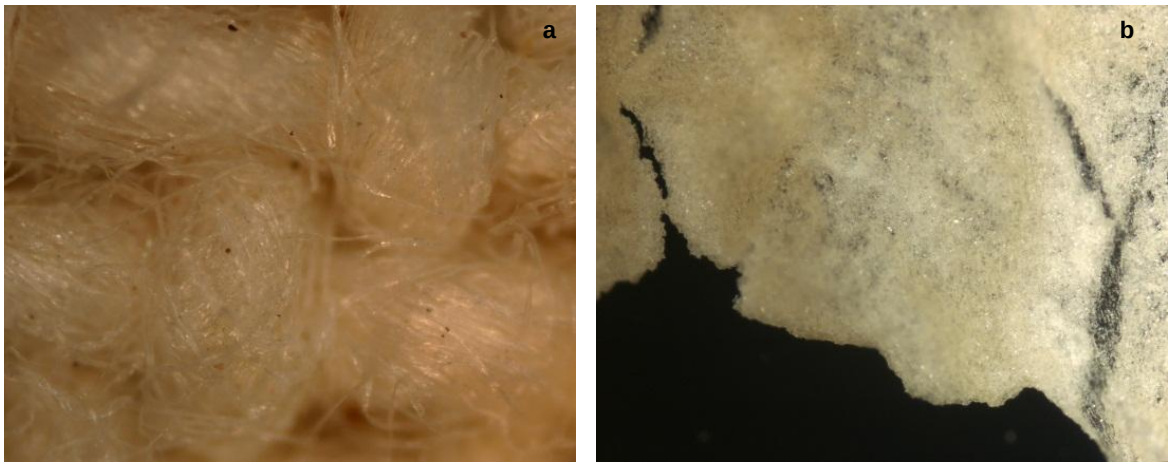


Fig.A7.1. Microphotography of the cotton canvas used for paint reconstructions for natural aging (a) and of the water soluble material removed during washing (b). (5x, reflected polarized light)

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Table A7.1. Summary of analyzes done in the cotton canvas used by Julião Sarmento.

Sample	FTIR	XRF
Unwashed canvas	Cellulose	**K**, Ca, Cl[¤], Fe°, Zn*, (Ar?)
Material extracted by water	Starch + CMC	**K**, Cl; (Ca); (S)
Washed canvas in an washing machine (2 washings at 60ºC)	—	**Ca**, Zn[#], Fe, (Ar?)
Washed canvas in distilled water (4 washings at 60ºC)	Cellulose	**Ca**, Fe, (K)

¤Cl can be a residue of textile processing, for example sodium hypochlorite (NaOCl) is one of the oldest industrial agents used for bleaching cotton.[124]

° During textile finishing cotton fibres are usually demineralized as they contain insoluble salts e.g. iron salts are naturally present in cotton.[124]

* This element was detected in only one of the five areas analyzed. It was related to brown spots found spread all over the canvas.

[#] Zn was found on all the five areas analyzed

Both cotton and startch are polysaccharides. Cotton has an approximate content of 85-90% of cellulose which consists of ß-D-glucose repeating units.[11] In turn starch is made of α-D-glucose and considerable chain branching occurs. it consists of two polysaccharides, amylose (a linear structure) and amylopectin (highly branched).[11] Amylose (about 20 %), is insoluble in cold water however amylopectin (about 80 %) is soluble in cold water.

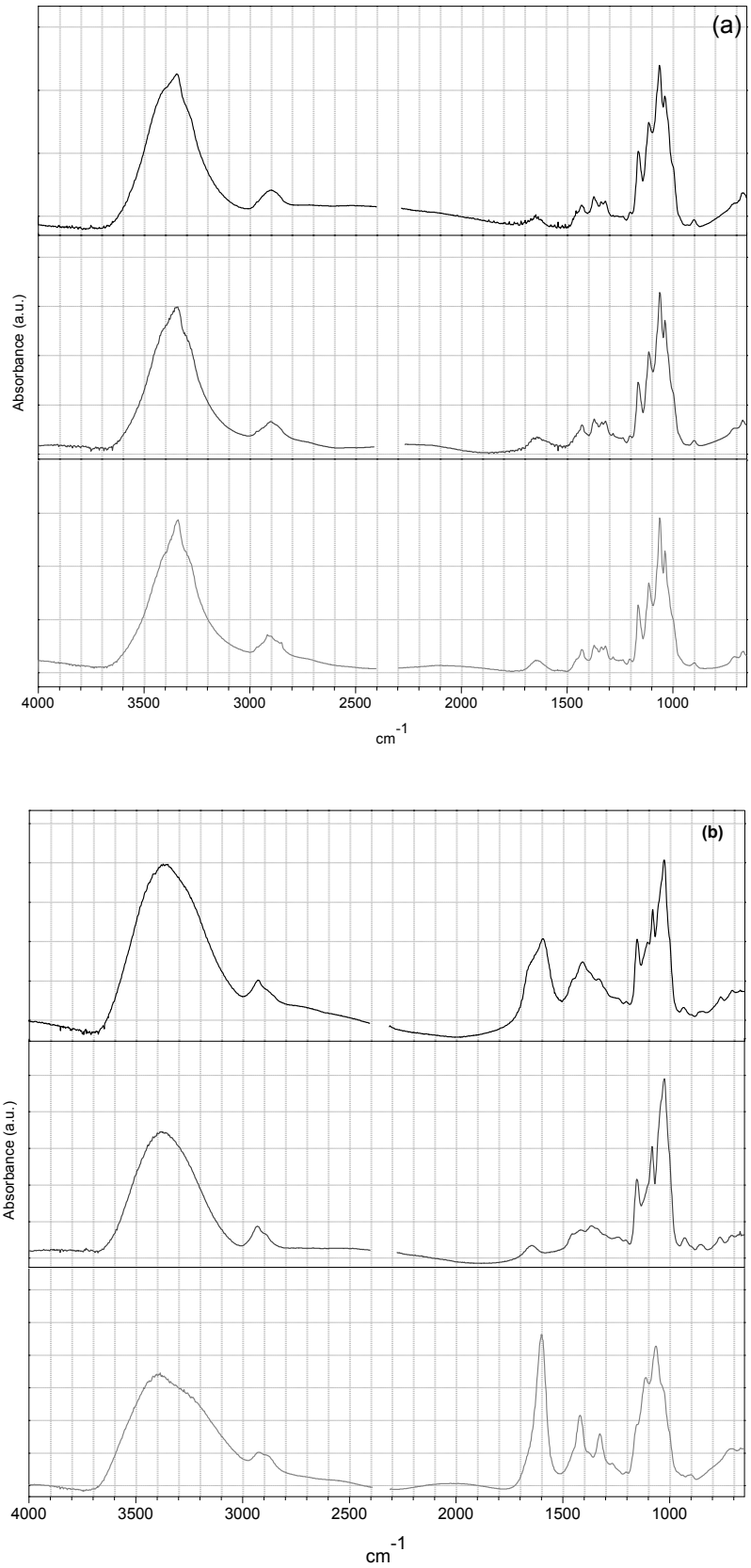

Fig.A7.2. (a) Infrared spectra of the cotton fibers: (—) cotton reference spectra; (—) unwashed cotton canvas; (—) washed cotton canvas;
(b) Infrared spectra of the water soluble material: (—) water soluble finishing material; (—) reference spectra of starch; (—) reference spectra of carboxymethyl cellulose.

Table A7.2. Band assignment in the spectra of the unwashed and washed canvas used in the natural aging experiment.

Wavenumber (cm^{-1})			Band assignment [153]
Unwashed canvas	**washed canvas**	**Cotton [153]**	
3340	3340	3335-3300	υOH free water
2900	2916	2900	υCH
—	2851	2850	υCH2
1641	1647	1635	Adsorbed water
1427	1429	1425-20	δCH
1370	1371	1370-65	δCH
1334	1336	1355-35	δCH_2 wagging
1317	1317	1315	δCH
1281	1281	1280	δCH_2 twisting
1201	1203	1200	δC-OH; δC-CH
1162	1162	1160-55	υC-C (ring)
1060	1060	1060-1050	υC(OH)
1036	1036	1025	υC(OH)
898	898	895	υC-O-C

Table A7.3. Band assignment in the spectra of the material removed from the cotton canvas with washing

Wavenumber (cm^{-1})			Band assignment
Extracted material	**Starch**	**CMC**	
3372	3361		υOH
2928	2930	2921	υCH
1641	1647	1600	intermolecular H-bond +C=O
1593	—	—	—
—	1450	1419	—
1408	1413	—	υCN
1333	1365	1326	—
1204	1204	—	—
1153	1152	—	υCO
1104	—	1111	—
1080	1081	1063	—
1027	1023	—	—
936	927	—	—
845	848	899	—
762	764	—	—
707	—	709	—

7.2. Colour changes: full colorimetry values

Table A7.4: L*, a*, b* and ΔE values measured during natural aging in the reproduction done by Sarmento with *Bizonte* and *Cenógrafa* white apllied on an unwashed cotton canvas.

	Workshop reproduction					
	Kept in the dark			Exposed to light		
	L*	a*	b*	L*	a*	b*
Time 0	91,15	-0,05	3,92	93,48	-0,12	3,97
	±1,68	±0,23	±0,31	±0,77	±0,10	±0,13
3	90,76	-0,04	3,80	93,49	0,49	3,62
	±1,76	±0,32	±0,29	±0,96	±0,16	±0,15
4	91,65	-0,02	4,12	93,18	0,06	4,00
	±1,94	±0,40	±0,47	±1,37	±0,03	±0,25
5	92,13	-0,07	3,91	93,90	0,03	3,98
	±1,09	±0,18	±0,19	±0,64	±0,06	±0,21
8	91,83	0,67	4,06	93,37	-0,21	3,56
	±1,30	±0,24	±0,25	±0,84	±0,12	±0,29
11	91,48	-0,02	4,16	93,49	0,47	4,18
	±1,43	±0,30	±0,34	±0,95	±0,06	±0,73
16	91,91	0,07	4,78	93,08	-0,45	4,70
	±1,26	±0,13	±0,30	±0,50	±0,25	±1,06
29	91,11	-0,04	3,94	92,80	-0,79	8,06
	±1,50	±0,19	±0,38	±0,67	±0,07	±1,90
Δ(L*, a*;b*)	-0,04	0,01	0,02	-0,68	-0,07	4,09
ΔE		0,05			4,15	

Table A7.5: L*, a*, b* and ΔE values measured during natural aging in reproductions containing lithopone.

	V7 + lithopone (70%-30%)									*Sabu + lithopone (70%-30%)*								
Time	**Washed canvas**			**Unwashed canvas**			**Glass-slide**			**Washed canvas**			**Unwashed canvas**			**Glass-slide**		
(Months)	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***
0	95.03	-0.34	2.60	93.48	-0.18	3.80	93.91	-0.63	1.59	94.35	-0.29	3.34	93.30	-0.27	5.09	93.25	-0.64	3.57
	±0.00	±0.04	±0.15	±0.10	±0.20	±0.47	±0.04	±0.04	±0.06	±0.02	±0.01	±0.15	±0.06	±0.01	±0.44	±0.00	±0.04	±0.16
1	94.65	-0.42	2.86	93.52	-0.19	3.23	93.47	-0.78	2.08	94.45	-0.31	3.18	93.25	-0.23	4.48	93.25	-0.64	3.71
	±0.15	±0.01	±0.09	±1.23	±0.25	±0.51	±0.09	±0.02	±0.00	±0.18	±0.02	±0.15	±0.36	±0.06	±0.57	±0.04	±0.05	±0.17
2	94.92	-0.58	3.48	94.32	-0.43	3.68	93.33	-0.99	3.01	94.38	-0.40	3.42	93.86	-0.31	4.76	93.24	-0.72	3.75
	±0.05	±0.00	±0.03	±0.02	±0.01	±0.02	±0.12	±0.04	±0.07	±0.22	±0.01	±0.18	±0.02	±0.01	±0.03	±0.17	±0.05	±0.21
4	94.95	0.18	4.50	94.49	0.27	4.06	93.54	-0.31	3.96	94.52	0.31	4.14	94.03	0.67	4.82	93.12	0.06	3.75
	±0.01	±0.03	±0.00	±0.06	±0.01	±0.01	±0.06	±0.02	±0.13	±0.12	±0.02	±0.22	±0.03	±0.01	±0.03	±0.33	±0.02	±0.15
5	94.82	-0.50	5.89	94.51	-0.31	5.01	93.65	-0.85	5.51	94.49	-0.33	5.20	94.05	-0.17	5.38	93.57	-0.48	4.31
	±0.01	±0.01	±0.04	±0.02	±0.00	±0.01	±0.02	±0.03	±0.14	±0.02	±0.01	±0.31	±0.02	±0.02	±0.05	±0.06	±0.03	±0.35
6	94.77	-0.53	6.26	94.42	-0.35	5.14	93.45	-0.92	5.93	94.41	-0.37	5.50	94.15	-0.20	5.26	93.61	-0.51	4.35
	±0.11	±0.01	±0.04	±0.04	±0.01	±0.07	±0.01	±0.01	±0.19	±0.02	±0.00	±0.30	±0.02	±0.01	±0.03	±0.00	±0.03	±0.36
8	94.18	-1.18	6.77	93.96	-0.95	5.59	92.80	-1.71	6.74	94.04	-0.93	5.77	93.79	-0.57	4.93	93.23	-0.88	3.85
	±0.01	±0.01	±0.22	±0.02	±0.01	±0.06	±0.04	±0.01	±0.17	±0.01	±0.02	±0.34	±0.00	±0.01	±0.02	±0.18	±0.02	±0.23
10	92.17	-1.27	8.14	93.89	-1.11	6.55	92.03	-1.81	8.38	93.52	-1.05	7.08	93.52	-0.65	5.45	93.21	-0.85	3.66
	±4.05	±0.01	±0.29	±0.01	±0.01	±0.03	±0.07	±0.05	±0.15	±0.01	±0.04	±0.41	±0.05	±0.02	±0.03	±0.00	±0.03	±0.28
12	94.09	0.85	8.89	94.08	0.55	7.15	92.52	0.48	9.12	93.83	0.83	8.01	93.62	0.65	5.75	93.46	-0.02	3.72
	±0.05	±0.12	±0.29	±0.03	±0.01	±0.11	±0.08	±0.06	±0.13	±0.02	±0.09	±0.45	±0.15	±0.02	±0.03	±0.01	±0.04	±0.17
17	93.04	-1.36	11.02	93.20	-1.46	10.25	91.63	-1.94	11.96	92.61	-1.16	10.70	92.82	-0.96	7.71	93.42	-0.82	4.02
	±0.06	±0.09	±0.36	±0.08	±0.04	±0.17	±0.13	±0.03	±0.25	±0.02	±0.07	±0.49	±0.11	±0.01	±0.01	±0.02	±0.03	±0.27
29	92.02	-0.91	12.86	91.87	-1.33	13.73	90.70	-1.59	14.22	91.09	-0.78	13.07	92.16	-1.24	11.79	91.87	-0.80	3.79
	±0.04	±0.02	±0.01	±0.03	±0.01	±0.02	±0.02	±0.12	±0.69	±0.03	±0.11	±0.56	±0.13	±0.02	±0.09	±0.49	±0.03	±0.09
Δ(L*, a*;b*)	**-3.01**	**-0.57**	**10.26**	**-1.61**	**-1.15**	**9.93**	**-3,21**	**-0.96**	**12.63**	**-3.26**	**-0.49**	**9.73**	**-1.14**	**-0.97**	**6.70**	**-1,38**	**-0.16**	**0.22**
ΔE		**10.71**			**10.13**			**13.07**			**10.27**			**6.87**			**1.41**	

Table A7.6: L*, a*, b* and ΔE values measured during natural aging in reproductions containing rutile titanium white and acrylic gypsum.

	V7 + lithopone (70%-30%) followed by Acrylic Gypsum (W&N)						*V7 + TiO_2 (70%-30%)*						*Sabu + TiO_2 (70%-30%)*					
Time	**Unwashed canvas**			**Glass-slide**			**Unwashed canvas**			**Glass-slide**			**Unwashed canvas**			**Glass-slide**		
(Months)	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***	**L***	**a***	**b***
0	96.49	-0.23	3.17	95.97	-0.53	2.49	96.20	-0.35	2.93	96.41	-0.28	3.78	96.57	-0.34	2.80	96.27	-0.30	3.34
	±0.01	±0.01	±0.04	±0.09	±0.05	±0.09	±0.16	±0.01	±0.02	±0.12	±0.01	±0.02	±0.03	±0.01	±0.02	±0.04	±0.01	±0.04
1	96.42	-0.20	3.13	95.85	-0.51	2.55	96.10	-0.35	3.22	96.45	-0.42	2.81	96.20	-0.33	3.50	95.94	-0.39	2.98
	±0.05	±0.02	±0.04	±0.02	±0.05	±0.05	±0.05	±0.01	±0.01	±0.03	±0.01	±0.01	±0.02	±0.00	±0.02	±0.17	±0.01	±0.02
2	96.53	0.68	3.01	95.99	0.20	2.37	96.24	-0.36	3.14	96.40	-0.43	2.81	96.53	-0.32	3.53	96.04	-0.41	2.96
	±0.01	±0.03	±0.06	±0.02	±0.10	±0.11	±0.04	±0.01	±0.02	±0.01	±0.00	±0.01	±0.01	±0.01	±0.03	±0.39	±0.01	±0.02
4	96.51	-0.03	3.38	96.02	-0.23	2.75	96.40	0.63	2.86	96.64	0.48	2.50	96.47	0.74	3.22	96.61	0.56	2.74
	±0.03	±0.01	±0.06	±0.04	±0.03	±0.07	±0.02	±0.01	±0.01	±0.01	±0.01	±0.01	±0.02	±0.01	±0.01	±0.03	±0.00	±0.02
5	96.53	-0.04	3.34	95.97	-0.24	2.72	96.38	-0.14	3.19	96.56	-0.20	2.80	96.25	-0.12	3.56	96.22	-0.17	3.16
	±0.00	±0.02	±0.06	±0.01	±0.03	±0.10	±0.08	±0.00	±0.03	±0.04	±0.01	±0.02	±0.10	±0.01	±0.03	±0.08	±0.01	±0.02
6	96.30	-0.24	3.20	95.73	-0.55	2.67	96.43	-0.16	3.10	96.52	-0.20	2.77	96.69	-0.15	3.51	96.49	-0.19	3.00
	±0.01	±0.04	±0.08	±0.02	±0.05	±0.07	±0.02	±0.01	±0.01	±0.04	±0.01	±0.01	±0.03	±0.01	±0.04	±0.07	±0.01	±0.01
8	96.03	-0.22	3.20	95.50	-0.54	2.65	96.22	-0.42	3.07	96.46	-0.46	2.86	96.27	-0.42	3.40	95.41	-0.46	3.09
	±0.01	±0.02	±0.06	±0.02	±0.04	±0.04	±0.01	±0.01	±0.01	±0.02	±0.02	±0.01	±0.04	±0.01	±0.03	±0.19	±0.01	±0.03
10	96.25	0.75	3.13	95.66	0.24	2.47	95.38	-0.40	3.19	96.29	-0.49	2.81	96.26	-0.43	3.34	96.21	-0.50	3.04
	±0.00	±0.07	±0.09	±0.02	±0.05	±0.06	±0.76	±0.04	±0.17	±0.01	±0.01	±0.01	±0.01	±0.01	±0.02	±0.02	±0.01	±0.02
12	96.06	-0.20	3.30	95.42	-0.35	2.83	96.32	0.61	2.84	95.83	0.51	2.62	96.57	0.73	3.28	96.53	0.55	2.84
	±0.28	±0.01	±0.05	±0.04	±0.26	±0.00	±0.04	±0.01	±0.03	±1.04	±0.01	±0.02	±0.03	±0.01	±0.03	±0.02	±0.00	±0.02
17	96.05	-0.17	3.35	95.49	-0.48	2.92	96.05	-0.43	3.50	96.16	-0.42	3.06	96.38	-0.49	2.91	95.72	-0.49	3.16
	±0.02	±0.02	±0.03	±0.04	±0.05	±0.12	±0.09	±0.01	±0.04	±0.04	±0.00	±0.01	±0.07	±0.01	±0.03	±0.23	±0.02	±0.01
29	95.55	-0.17	3.60	95.42	-0.53	3.28	95.83	-0.45	3.29	95.26	-0.48	3.12	95.69	-0.43	3.67	95.96	-0.51	3.22
	±0.00	±0.03	±0.03	±0.01	±0.04	±0.29	±0.02	±0.01	±0.02	±0.04	±0.01	±0.02	±0.02	±0.02	±0.02	±0.08	±0.01	±0.03
Δ(L*, a*;b*)	**-0.94**	**0.06**	**0.43**	**-0.55**	**0.00**	**0.79**	**-0.37**	**-0.1**	**0.36**	**-1.15**	**-0.2**	**-0.66**	**-0.88**	**-0.09**	**0.87**	**-0.31**	**-0.21**	**-0.12**
ΔE		**1.04**			**0.96**			**0.53**			**1.34**			**1.24**			**0.39**	

Table A7.7: L*, a*, b* and ΔE values measured during natural aging in reproductions containing *V7* and *Cenógrafa* white with different layer thickness.

	V7 + lithopone (70%-30%)					
	Thicker sample			**Thinner sample**		
Time	**Unwashed canvas**			**Unwashed canvas**		
(Months)	**L***	**a***	**b***	**L***	**a***	**b***
0	94,66	-1,03	6,94	93,77	-0,93	5,79
	±0,28	±0,03	±0,13	±0,18	±0,06	±0,07
1	94,63	-1,19	8,27	94,85	-1,19	7,22
	±0,28	±0,02	±0,04	±0,06	±0,00	±0,06
2	94,32	-1,16	9,93	94,45	-1,22	8,62
	±0,06	±0,01	±0,03	±0,09	±0,01	±0,04
4	94,34	1,57	10,97	94,88	1,14	9,41
	±0,09	±0,01	±0,04	±0,08	±0,01	±0,06
5	94,45	-0,74	12,65	94,43	-0,81	11,05
	±0,02	±0,01	±0,03	±0,03	±0,01	±0,02
6	94,33	-0,69	13,12	94,50	-0,79	11,36
	±0,04	±0,01	±0,02	±0,02	±0,01	±0,03
8	93,33	-1,00	12,75	93,71	-1,23	11,07
	±0,27	±0,01	±0,01	±0,02	±0,02	±0,01
10	92,25	-0,56	13,50	92,81	-0,86	12,16
	±0,09	±0,01	±0,03	±0,14	±0,01	±0,02
12	92,23	3,02	14,67	93,52	2,34	12,91
	±0,05	±0,01	±0,01	±0,11	±0,02	±0,02
17	91,10	0,47	15,44	91,76	-0,02	14,34
	±0,09	±0,04	±0,03	±0,05	±0,01	±0,02
29	90,19	0,93	15,81	90,31	0,43	14,71
	±0,03	±0,04	±0,07	±0,17	±0,08	±0,01
Δ(L*, a*;b*)	**-4,47**	**1,96**	**8,87**	**-3,46**	**1,36**	**8,92**
ΔE		**10,12**			**9,66**	

7.3. Infrared analyzes: full results

Table A7.8: Infrared absorptions normalized for the C=O stretching for the samples containing *Cenógrafa* white subjected to natural aging.

		CH			C=O	1433	1373	CO	1123	1073	1022
***V7* + lithopone**	glass slide unaged	0.15 ± 0.04	0.15 ± 0.04	0.08 ± 0.03	1.00	—	—	0.88 ± 0.06	0.44 ± 0.04	0.48 ± 0.07	0.32 ± 0.03
	glass slide aged	0.11 ± 0.02	0.09 ± 0.01	0.06 ± 0.01	1.00	—	—	0.83 ± 0.06	0.44 ± 0.10	0.50 ± 0.12	0.35 ± 0.12
	unwashed canvas unaged	0.13 ± 0.01	0.12 ± 0.02	0.08 ± 0.02	1.00	—	—	0.78 ± 0.01	0.34 ± 0.03	0.38 ± 0.04	0.25 ± 0.02
	unwashed canvas aged	0.10 ± 0.02	0.11 ± 0.10	0.04 ± 0.02	1.00	—	—	0.79 ± 0.01	0.38 ± 0.03	0.42 ± 0.04	0.28 ± 0.03
	washed canvas unaged	0.11 ± 0.01	0.10 ± 0.01	0.06 ± 0.01	1.00	—	—	0.78 ± 0.03	0.35 ± 0.02	0.40 ± 0.03	0.23 ± 0.02
	washed canvas aged	0.11 ± 0.01	0.10 ± 0.01	0.06 ± 0.02	1.00	—	—	0.77 ± 0.01	0.35 ± 0.01	0.41 ± 0.02	0.25 ± 0.01
***V7* + TiO_2**	glass slide unaged	0.14 ± 0.01	0.13 ± 0.01	0.08 ± 0.00	1.00	0.10 ± 0.02	0.31 ± 0.01	0.73 ± 0.01	0.20 ± 0.04	0.19 ± 0.05	0.26 ± 0.05
	glass slide aged	0.11 ± 0.04	0.11 ± 0.04	0.07 ± 0.04	1.00	0.11 ± 0.01	0.31 ± 0.01	0.73 ± 0.02	0.17 ± 0.04	0.15 ± 0.04	0.22 ± 0.03
	unwashed canvas unaged	0.11 ± 0.01	0.10 ± 0.01	0.05 ± 0.01	1.00	0.11 ± 0.00	0.32 ± 0.02	0.73 ± 0.04	0.17 ± 0.04	0.15 ± 0.05	0.24 ± 0.05
	unwashed canvas aged	0.21 ± 0.03	0.22 ± 0.03	0.14 ± 0.03	1.00	0.14 ± 0.02	0.32 ± 0.03	0.71 ± 0.04	0.22 ± 0.07	0.20 ± 0.07	0.27 ± 0.07

Table A7.9: Infrared absorptions normalized for the C=O stretching for the samples containing *Sabu* and *Cenógrafa* white subjected to natural aging.

		CH			**C=O**			**CO**	**1123**	**1073**	1022
***Sabu* + Lithopone**	glass slide unaged	0.11 ± 0.01	0.11 ± 0.01	0.06 ± 0.00	1.00	—	—	0.76 ± 0.03	0.40 ± 0.03	0.49 ± 0.04	0.26 ± 0.03
	glass slide aged	*0.16 ± 0.02*	*0.16 ± 0.03*	*0.11 ± 0.02*	*1.00*	—	—	*0.80 ± 0.03*	*0.41 ± 0.04*	*0.48 ± 0.04*	*0.29 ± 0.02*
	unwashed canvas unaged	0.13 ± 0.02	0.12 ± 0.03	0.07 ± 0.02	1.00	—	—	0.78 ± 0.02	0.40 ± 0.05	0.48 ± 0.04	0.30 ± 0.06
	unwashed canvas aged	*0.16 ± 0.03*	*0.15 ± 0.03*	*0.10 ± 0.03*	*1.00*	—	—	*0.79 ± 0.01*	*0.43 ± 0.01*	*0.50 ± 0.01*	*0.28 ± 0.02*
	washed canvas unaged	0.12 ± 0.02	0.11 ± 0.01	0.07 ± 0.02	1.00	—	—	0.77 ± 0.05	0.41 ± 0.04	0.49 ± 0.03	0.25 ± 0.02
	washed canvas aged	*0.09 ± 0.02*	*0.09 ± 0.02*	*0.04 ± 0.01*	*1.00*	—	—	*0.78 ± 0.02*	*0.38 ± 0.03*	*0.45 ± 0.02*	*0.28 ± 0.03*
***Sabu* + TiO_2**	glass slide unaged	0.15 ± 0.02	0.15 ± 0.02	0.10 ± 0.03	1.00	0.13 ± 0.00	0.31 ± 0.02	0.72 ± 0.03	0.21 ± 0.03	0.20 ± 0.02	0.27 ± 0.03
	glass slide aged	—	*0.14 ± 0.00*	*0.06 ± 0.01*	*1.00*	*0.12 ± 0.01*	*0.29 ± 0.02*	*0.69 ± 0.03*	*0.19 ± 0.06*	*0.19 ± 0.07*	*0.27 ± 0.07*
	unwashed canvas unaged	0.13 ± 0.01	0.13 ± 0.00	0.07 ± 0.00	1.00	0.15 ± 0.01	0.32 ± 0.01	0.73 ± 0.01	0.26 ± 0.01	0.25 ± 0.02	0.32 ± 0.02
	unwashed canvas aged	*0.13 ± 0.05*	*0.12 ± 0.05*	*0.08 ± 0.04*	*1.00*	*0.13 ± 0.03*	*0.33 ± 0.02*	*0.76 ± 0.03*	*0.22 ± 0.04*	*0.20 ± 0.04*	*0.23 ± 0.03*

Table A7.10: Infrared absorptions normalized for the C=O stretching for the samples containing *Bizonte* and *Cenógrafa* white subjected to natural aging.

	CH			C=O	CO
Workshop sample kept in the dark	0.09 ± 0.01	0.09 ± 0.01	0.06 ± 0.02	1.00	0.82 ± 0.05
Workshop sample kept in the light White areas	0.10 ± 0.02	0.10 ± 0.02	0.06 ± 0.01	1.00	0.89 ± 0.03
Workshop sample kept in the light Yellowed areas	*0.15 ± 0.01*	*0.14 ± 0.02*	*0.11 ± 0.03*	*1.00*	*0.93 ± 0.05*
Workshop sample kept in the dark White areas	0.09 ± 0.01	0.09 ± 0.01	0.06 ± 0.02	1.00	0.83 ± 0.05
Workshop sample kept in the dark Yellowed areas	*0.10 ± 0.02*	*0.10 ± 0.02*	*0.07 ± 0.03*	*1.00*	*0.85 ± 0.06*

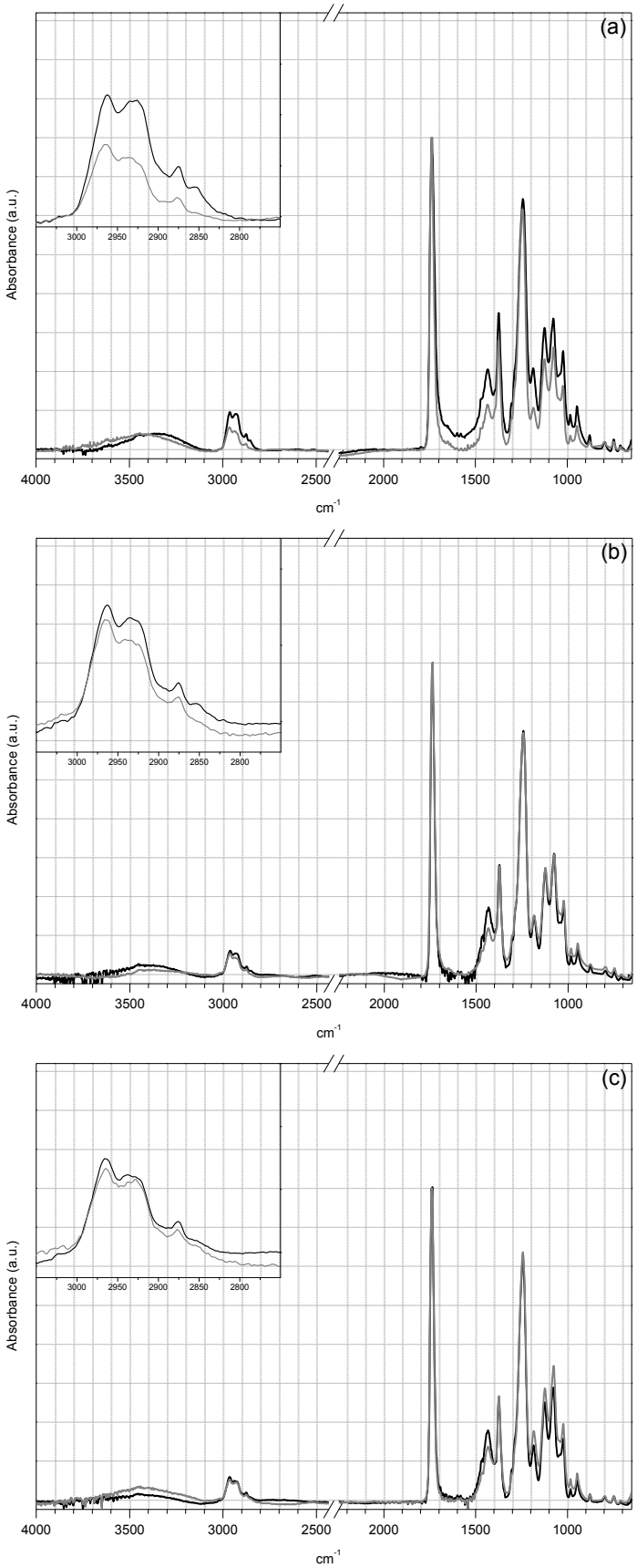

Fig. A7.3. Infrared spectra of the pigmented samples containing the *V7* emulsion and lithopone before (—) and after (—) natural aging (a) applied on glass-slide (b) unwashed canvas and (c) on washed canvas.

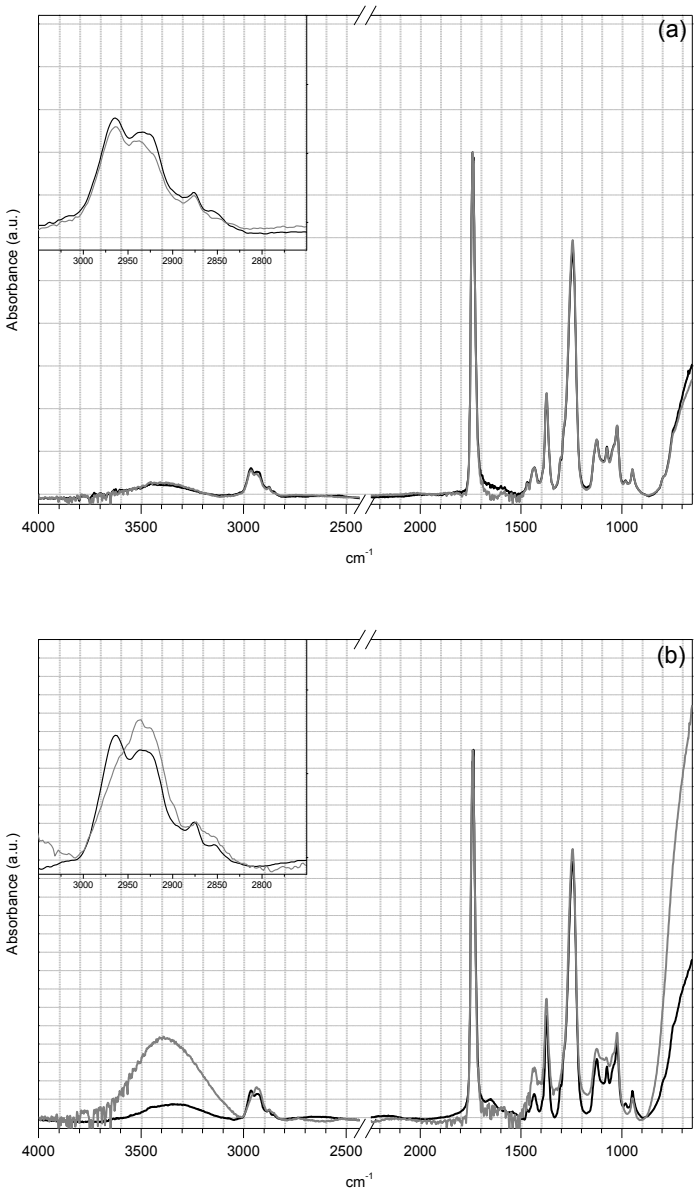

Fig. A7.4. Infrared spectra of the pigmented samples containing the *Vulcano V7* emulsion and rutile titanium white before (—) and after (—) natural aging (a) applied on glass-slide (b) unwashed canvas

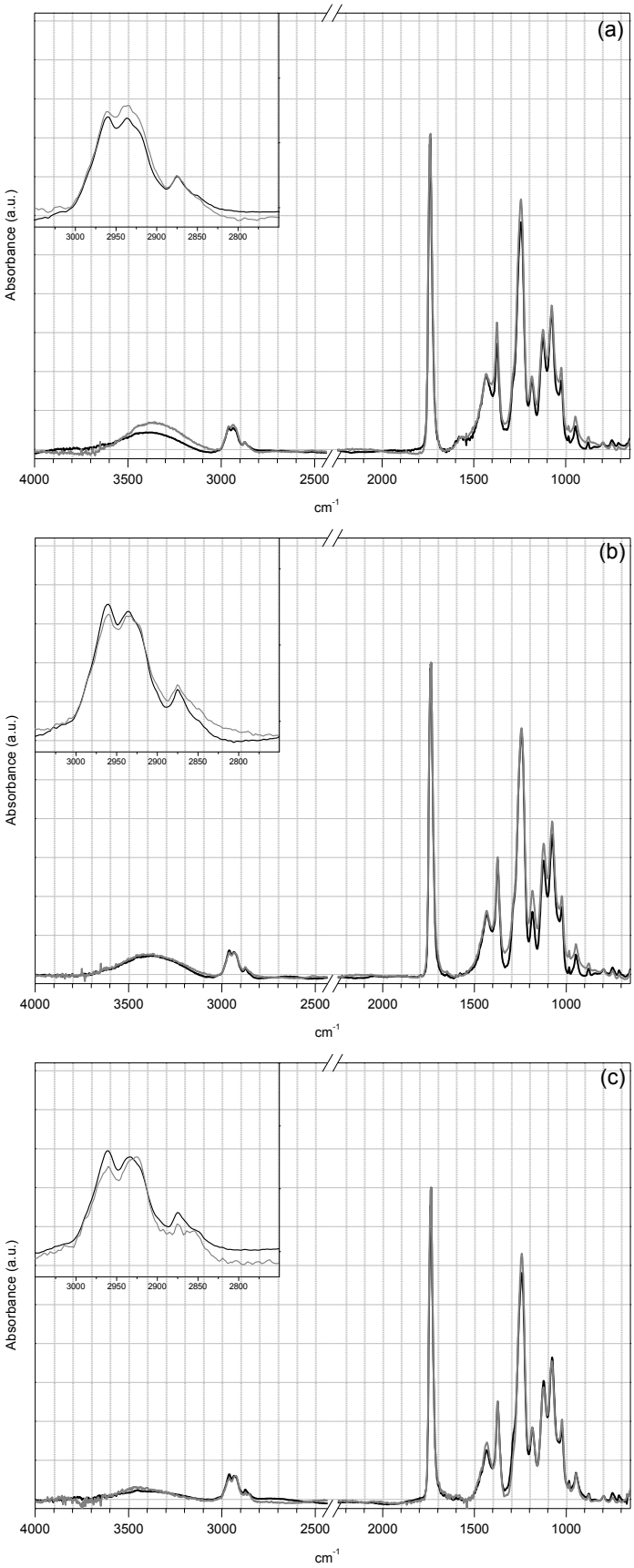

Fig. A7.5. Infrared spectra of the pigmented samples containing the*Sabu* emulsion and lithopone before (—) and after (—) natural aging (a) applied on glass-slide (b) unwashed canvas and (c) on washed canvas

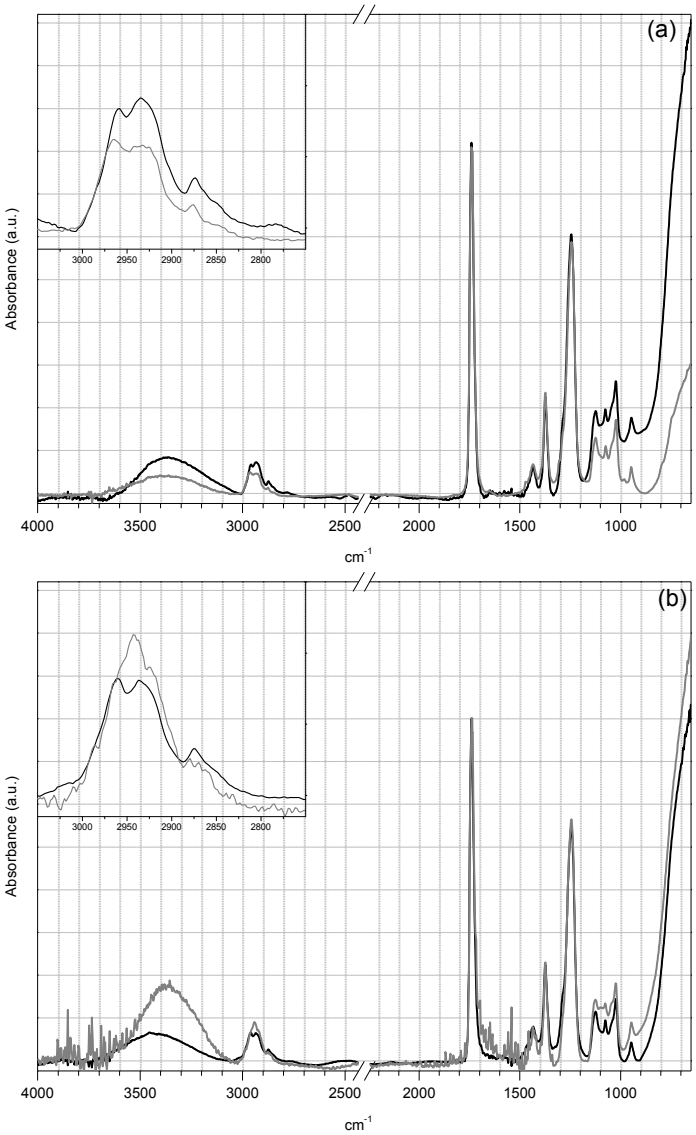

Fig. A7.6. Infrared spectra of the pigmented samples containing the *Sabu* emulsion and rutile titanium white before (—) and after (—) natural aging (a) applied on glass-slide (b) unwashed canvas

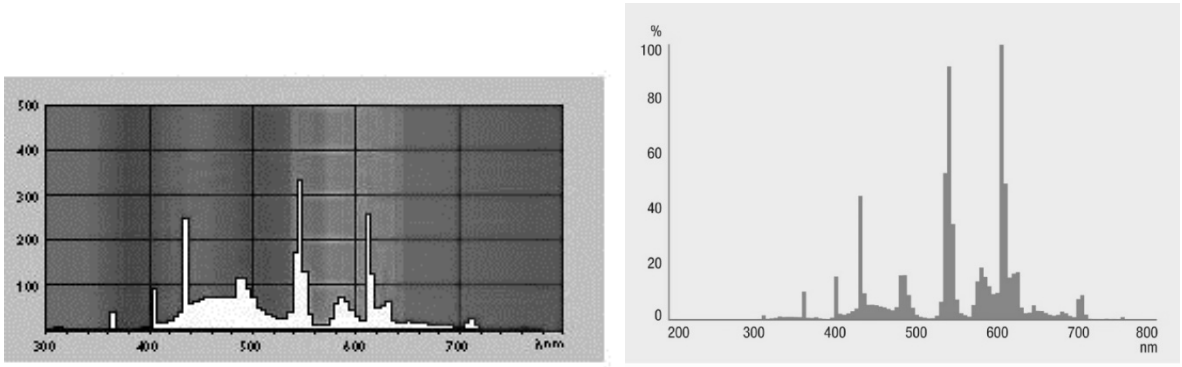

Fig. A7.7. Spectral power distribution curves for the two light sources used in the laboratory (a) *Philips Master TL-D* 58W/840 (b) *OSRAM* L58W/840 (information provided by the manufacturers).

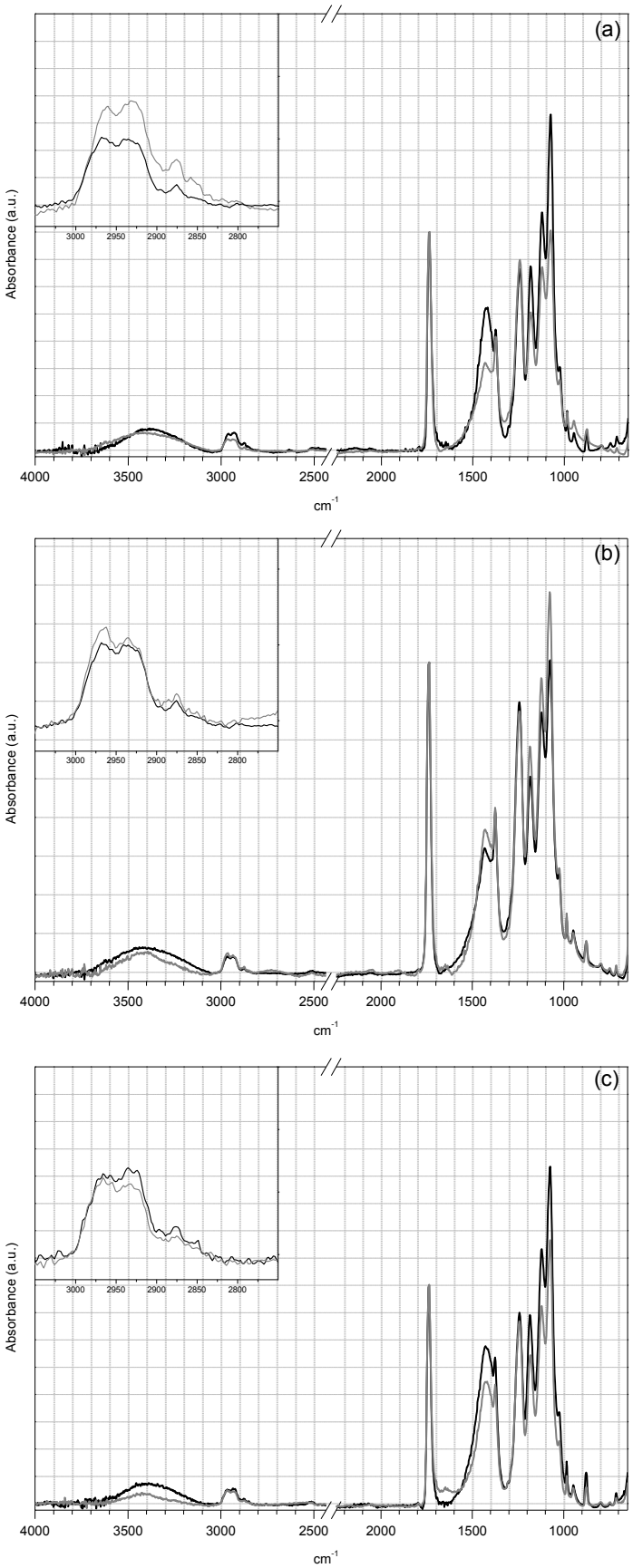

Fig. A7.8. ATR spectra of the pigmented samples containing the *Bizonte* emulsion white *Cenógrafa* white before (—) and after (—) natural aging (a) kept in the dark (b) exposed to light (c) kept in the dark after yellowing when exposed to light.

Appendix VIII. Cleaning Synthetic paints

8.1. Full results for cleaning tests in artificially aged samples

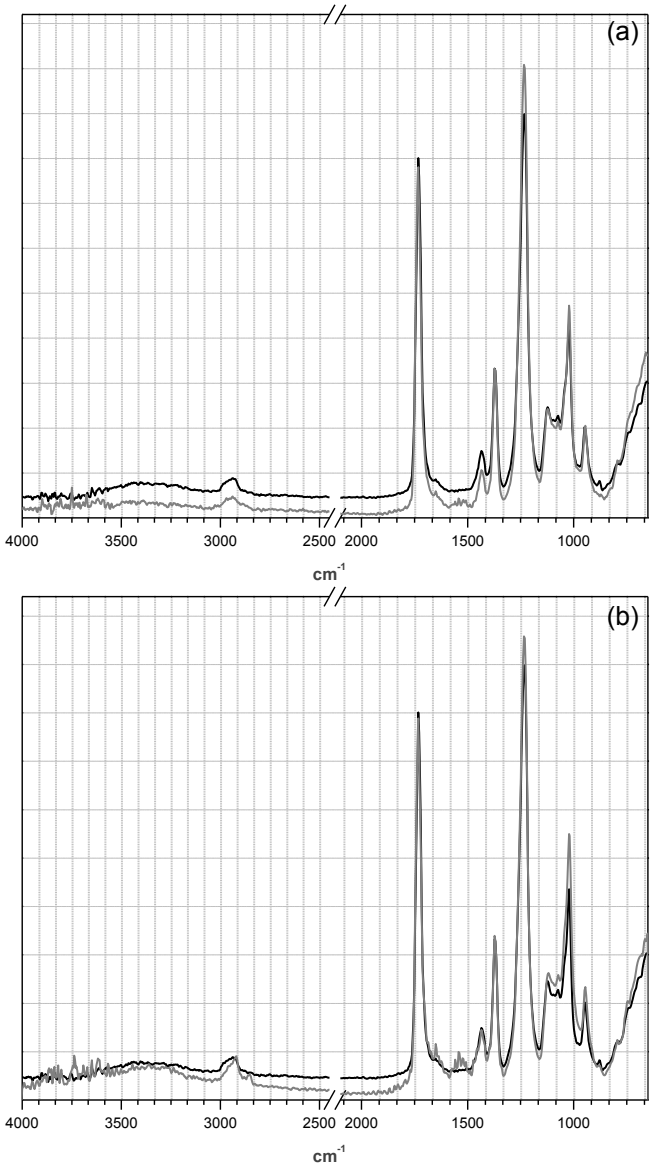

Fig. A8.1: ATR spectra of the paint's surface (a) control sample (—) and after immersion in white spirit (—); (b) control sample (—) and after cleaning with Akapad (—)

8.2. Conductivity

Solutions of non-electrolytes contain neutral molecules or atoms and are no-conductors. Solutions of electrolytes are good conductors due to the presence of anions and cations.[154] It is possible to distinguish between free ions from associated and covalently bonded species by conductivity measurements, because only free ions are responsible for electrical conductivity in solutions.[154]

The conductivity of a cleaning solution can have an effect on the physical structure of a paint film. For example if conductivity is too high, the surface may be damaged through ionic interactions with paint constituents.[146] Other risks of using hypertonic solutions (e.g. conductivities higher than about 10-20x of the isotonic condition of the painting surface) are generally avoided because of the risk of swelling, softening and the associated trapping and clearance problem of the cleaning materials into the softened paint films.[155]

Ideally isotonic cleaning solutions (e.g. same concentration of ions that are present in the painted surface) generally cause the least swelling and therefore have less damaging effects on the paint films. However, Wolbers recommends using cleaning solutions constructed close (e.g.≈10 to 20x) to the conductivity of the surface since these are considered reasonable in terms of risk. .[155]

As far as conductivity is concerned current maximum limits for cleaning solutions intended for oil paints are 2mS/cm. For the acrylic emulsion paint the isotonic values are 0.3-6 mS/cm due to the presence of ionic additives as for example surfactants and thickeners. (Wolbers, Archetype, 2012, procurar referência original) Solutions with TAC tend to decrease the swelling of the paint films probably in part due to the relatively high ionic strength of this solution.[133] There is a slight decrease of swelling with increased solution conductivity. Recommendations for the conductivity level of aqueous cleaning solutions appropriate for acrylic emulsion paint films have already been determined and are different from the values for oil paint. Within the studied range of 2 to 9 mS/cm the lowest swelling combination was found to be a pH of 4.0 and a conductivity of 7.0 mS/cm.[133] Conductivity is primarily dependent on the composition of the soiling layer, however the slight variations observed with different pigment contents warrant further investigation.[132]